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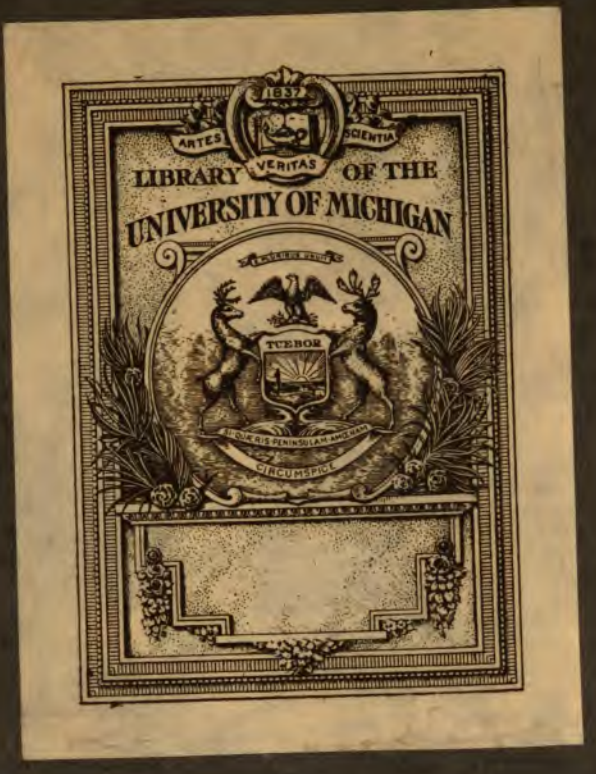
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MANGANESE IN WATER SUPPLIES

BY

HARRY PEACH CORSON
B. S. New Hampshire College, 1910
M. S. University of Illinois, 1912

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MANGANESE IN WATER SUPPLIES

By H. P. Corson.

INTRODUCTION

Water supplies containing manganese have been considered uncommon in the United States, and determinations of manganese are made in but few laboratories as a part of the general routine work of water analysis. Even in the selection of a water supply for a community the content of manganese is seldom considered. In April, 1911, the attention of the Illinois State Water Survey was called to a serious incrustation which had formed in the city water system of Mount Vernon, Illinois.[1] An analysis showed that this incrustation contained 4.4 to 8.8 per cent and that the original water contained 0.6 part per million of manganese. Manganese was found later, in a number of other water supplies both public and private, of the State.

Manganese in a water supply is objectionable because it deposits in water pipes a dark incrustation, which in some pipes is so extensive as to cause complete stoppage. It stains plumbing fixtures a dark color due to the separation of the dioxide. It also stains fabrics yellow or brown when water containing it is used in the laundry. In these respects waters containing manganese resemble those which contain iron, but the deposits are darker and more difficult to remove than those produced by waters which contain iron. The present investigation was undertaken on account of the economic importance of this subject. The problem has been studied from the standpoints of the quantitative determination of manganese, its occurrence and distribution in natural waters, and its removal from water supplies.

DETERMINATION OF MANGANESE IN WATER

Previous Investigations

Theoretically, it might seem that any accurate method for the determination of manganese in substances could be successfully applied to the determination of the element in water. Many methods are, however, wholly impracticable. Manganese occurs in water in relatively small amounts, usually only a small fraction of a milligram

[1]Corson, H. P., Occurrence of manganese in the water supply and in an incrustation in the water mains at Mount Vernon, Illinois: Illinois Univ. Bull., Water-Survey Series 10, 57-65 (1913).

per liter. In some waters several milligrams per liter are found, but those in which more than 10 milligrams per liter of the element are encountered are very uncommon. Most other salts are present in natural waters in amounts many times as great as the salts of manganese. These conditions eliminate some of the accurate standard gravimetric and volumetric methods for the determination of manganese. If they are used, under most conditions, large volumes of water must be evaporated in order to procure a sufficient quantity of the element for determination. In complete analysis of the mineral content of water samples these procedures may not be seriously objectionable, but in rapid work, such as the analytical control of a manganese-removal plant, they would be wholly impracticable.

Several water analysts have recommended volumetric or gravimetric methods for manganese.

Lührig and Becker[1] report satisfactory results in applying Knorre's[2] persulphate peroxide method to the determination of manganese in water. If the water contains less than 10 milligrams per liter of manganese, however, they state that it must be concentrated by evaporation. Klut[3] also recommends the same method for waters whose content of manganese is more than 10 milligrams per liter. He states, however, that 5 to 10 liters of the sample should be used. Prescher[4] recommends that the manganese be precipitated with potassium chlorate from a one-liter sample as manganese dioxide after concentration with nitric acid. The precipitated manganese dioxide is then dissolved in standard oxalic acid, the excess of which is determined by titrating with potassium permanganate. He states that the amount of manganese found must be increased by 10 per cent in order to give a correct value. Noll[5] precipitates the manganese as the dioxide in an ammoniacal solution with bromine water. This precipitate is then treated with hydrochloric acid and potassium iodide, and the liberated iodine is titrated with sodium thiosulphate. Results which were in good agreement with the theoretical values were obtained on some artificially prepared manganese waters. The volume of sample used was 500 cubic centimeters. All these methods, however, have found little favor and colorimetric methods are in general use. Colorimetric methods for the determination of manganese de-

[1]Lührig, H., and Becker, W., Zur Bestimmung des Mangans im Trinkwasser: Pharm. Zentralhalle, 48, 137-42 (1907).

[2]Knorre, G. von, Ueber eine neue Methode zur Manganbestimmung: Z. angew. Chem., 14, 1149-62 (1901).

[3]Klut, H., Nachweis und Bestimmung von Mangan im Trinkwasser: Mitt. kgl. Prufungsamt. Wasserversorg. Abwasserbeseit., 12, 182-94 (1909).

[4]Prescher, Johannes, Zur Bestimmung des Mangans im Trinkwasser: Pharm. Zentralhalle, 47, 799-802 (1906).

[5]Noll, H., Manganbestimmung in Trinkwasser: Z. angew. Chem., 20, 490-2 (1907).

pend on oxidation of the manganous salt to permanganate and comparison of the color produced thereby with standards of known content of permanganate. Three oxidizing agents, lead peroxide (PbO_2), sodium bismuthate ($NaBiO_3$), and ammonium persulphate ($(NH_4)_2S_2O_8$) have been used for the oxidation.

The committee on standard methods of water analysis[1] permits use of the bismuthate and the lead-peroxide methods for the determination of amounts of manganese less than 10 milligrams per liter but recommends Knorre's[2] volumetric persulphate method if more than that amount is present.

In the Bureau of Chemistry, U. S. Department of Agriculture[3], the colorimetric persulphate method is used. It was found on inquiry, that no water chemists use the lead-peroxide method. As several methods are used for determining manganese in water and some literature has accumulated concerning their accuracy and sources of error it seemed advisable to make a careful comparison of them for the proposed revision of the report of the committee on standard methods of water analysis.[4] Accordingly the lead-peroxide method, the sodium-bismuthate method, and the ammonium-persulphate method were carefully compared.

Experimental Studies

PREPARATION OF SOLUTIONS

Solutions of manganous chloride, potassium permanganate, and manganous sulphate, of known content of manganese were prepared.

Manganous chloride.—A standard solution of manganous chloride was prepared by dissolving approximately 32 grams of pure manganous chloride ($MnCl_2.4H_2O$) in a liter of distilled water. To obtain pure manganous chloride a solution of about 200 grams of Baker's Analyzed manganous chloride in one liter of distilled water was boiled with a small amount of manganese carbonate prepared by adding sodium carbonate to a portion of the original solution, filtering, and washing the precipitate. Possible traces of iron, aluminium, and chromium were thus removed. The mixture was then filtered, after which the filtrate was treated with ammonium sulphide to remove copper, lead, and other heavy metals. The solution was then acidified with hydrochloric acid and boiled to remove hydrogen sul-

[1] Standard methods for the examination of water and sewage, Am. Pub. Health Assoc., New York, 2nd ed., 49-51 (1912).

[2] Knorre, G. von, Ueber eine neue Methode zur Manganbestimmung: Z. angew. Chem., 14, 1149-62 (1901).

[3] Colorimetric determination of manganese: in Proc. 28th Ann. conv. Assoc. Off. Agr. Chemists, U. S. Agri. Dept., Bur. Chem. Bull. 152, 78-79 (1912).

[4] To be published in 1916.

phide, after which it was filtered. A small amount of copper, which was present, was thus removed. An excess of sodium carbonate was next added, and the manganous carbonate was separated by filtration and washed free from chlorides. Most of this precipitate was then dissolved in hydrochloric acid. A small portion of that which did not dissolve was added to the solution, and the mixture was boiled and filtered. Crystalline manganous chloride was obtained on evaporation. The chloride in the standard solution of this was determined gravimetrically, and the amount of manganese was calculated from that result. Manganese was also directly determined by evaporating to dryness a 50 cubic centimeter portion of the solution with sulphuric acid, heating, and weighing as manganous sulphate. Gooch and Austin[1] have shown that this method is accurate. The average of triplicate determinations by each method gave the following results:

By determining chlorine as silver chloride one cubic centimeter contains 1.604 milligrams of chlorine and 1.245 milligrams of manganese.

By determining manganese as manganous sulphate one cubic centimeter contains 1.254 milligrams of manganese.

The mean of these two values, 1.250 milligrams of manganese, was taken as the strength of the solution, which was then diluted to one-tenth of its original strength, so that one cubic centimeter contained 0.125 milligram of manganese.

Potassium permanganate.—For the preparation of standards of permanganate by simple dilution a standard solution was prepared by dissolving in one liter of water 0.2880 gram of Kahlbaum's potassium permanganate that had been crystallized twice from double distilled water and dried over sulphuric acid. The content of one cubic centimeter of this solution was, therefore, assumed to be 0.100 milligram of manganese.

Manganous sulphate.—Dilute solutions of permanganate are not very stable.[2] In order to check their value and to have standards prepared exactly as the sample was treated 0.2880 gram of potassium permanganate dissolved in water was reduced to manganous sulphate by heating with sulphuric acid and a slight excess of oxalic acid, after which the solution was diluted to one liter. One cubic centimeter of this solution contained, therefore, 0.100 milligram of manganese.

[1]Gooch, F. A., and Austin, Martha, Die Bestimmung des Mangans als Sulfat und als Oxyd: Z. anorg. Chem., 17, 264-71 (1898).

[2]Morse, H. N., Hopkins, A. J., and Walker, M. S., The reduction of permanganic acid by manganese superoxide: Am. Chem. J., 18, 401-19 (1896).

LEAD-PEROXIDE METHOD

The lead-peroxide method, first described by Crum[1], has been used for a long time in iron and steel work. It has, however, been used only to limited extent in water analysis, and it has been largely supplanted by the bismuthate and persulphate methods. Of twelve investigators who have worked on the determination of manganese in water during the past ten years Klut[2] alone recommends this method. The majority favor the persulphate method and the bismuthate method seems to be second in popularity. No one, however, appears carefully to have compared the three methods. The material embodied in the section dealing with manganese in the report of the committee[3] appears to have been based entirely upon the work of Klut[2] and of R. S. Weston.[4]

TABLE 1.—FIRST SERIES OF DETERMINATIONS OF MANGANESE BY THE LEAD-PEROXIDE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN DISTILLED WATER COMPARED WITH DILUTE STANDARD SOLUTION OF POTASSIUM PERMAGANATE.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard permanganate.	Determined content.	Theoretical content.	Excess of determined over theoretical value.
0.0	0.0	0.00	0.00	±0.00
.2	.0	.00	.025	— .025
.2	.0	.00	.025	— .025
.4	.2	.02	.050	— .03
.4	.2	.02	.050	— .03
.6	.3	.03	.075	— .045
.6	.4	.04	.075	— .035
.8	.7	.07	.100	— .03
.8	.6	.06	.100	— .04
1.0	1.0	.10	.125	— .025
1.0	1.0	.10	.125	— .025
1.2	1.2	.12	.150	— .03
1.2	1.3	.13	.150	— .02
1.5	1.8	.18	.187	— .007
1.5	1.8	.18	.187	— .007
2.0	2.5	.25	.250	± .00
2.0	2.3	.23	.250	— .02
2.5	2.8	.28	.312	— .032
2.5	2.5	.25	.312	— .062
3.0	3.5	.35	.375	— .025
3.0	3.5	.35	.375	— .025
3.5	4.0	.40	.438	— .038
3.5	4.0	.40	.438	— .038
4.0	4.5	.45	.500	— .050
4.0	5.0	.50	.500	± .000
		Mean		— .027

[1]Crum, Walter, Empfindliches Prüfungsmittel auf Mangan: Ann., 55, 219-20 (1845).

[2]Klut, H., Nachweis und Bestimmung von Mangan im Trinkwasser: Mitt. kgl. Prüfungsamt. Wasserversorg. Abwasserbeseit., 12, 182-94 (1909).

[3]Standard methods for the examination of water and sewage, Am. Pub. Health Assoc., New York, 2nd ed., 49-51 (1912).

[4]Weston, R. S., The determination of manganese in water: J. Am. Chem. Soc., 29, 1074-8 (1907).

The first series of experiments with the lead-peroxide method was carried out according to the following procedure. Different amounts of the standard manganous-chloride solution were diluted with distilled water, and evaporated in beakers with two or three drops of sulphuric acid until white fumes appeared. They were then diluted with water, acidified with 10 cubic centimeters of dilute nitric acid free from brown oxides of nitrogen, boiled down to a volume of 50 cubic centimeters, treated with 0.5 gram of lead peroxide, and boiled for five minutes. It was then filtered through an asbestos mat in a Gooch crucible, which had been ignited, treated with permanganate, and washed with water. The filtrate was transferred to a Nessler tube and the color was compared immediately with standards made by diluting the standard solution of potassium permanganate with water acidified with sulphuric acid. The results, shown in Table 1, indicate that the determined amounts of manganese were nearly all lower than the amounts actually present. The mean difference in the twenty-five determinations was 0.027 milligram.

In order to check the possibility of error due to possible difference in content of manganese between the solutions of manganous

TABLE 2.—SECOND SERIES OF DETERMINATIONS OF MANGANESE BY THE LEAD-PEROXIDE METHOD.

SOLUTIONS OF KNOWN CONTENT OF POTASSIUM PERMANGANATE IN DISTILLED WATER COMPARED WITH DILUTE STANDARD SOLUTION OF POTASSIUM PERMANGANATE.

Cubic centimeters of solution.		Milligrams of manganese.		
Potassium permanganate.	Standard permanganate.	Determined content.	Theoretical content.	Excess of determined over theoretical value.
0.0	0.0	0.00	0.00	± .00
.2	.0	.00	.02	— .02
.2	.0	.00	.02	— .02
.4	.15	.015	.04	— .025
.4	.10	.01	.04	— .03
.6	.3	.03	.06	— .03
.6	.3	.03	.06	— .03
.8	.4	.04	.08	— .04
.8	.5	.05	.08	— .03
1.0	.8	.08	.10	— .02
1.0	.8	.08	.10	— .02
1.2	1.0	.10	.12	— .02
1.2	.9	.09	.12	— .03
1.5	1.2	.12	.15	— .03
1.5	1.2	.12	.15	— .03
2.0	1.8	.18	.20	— .02
2.0	2.0	.20	.20	± .00
2.5	2.2	.22	.25	— .03
2.5	2.2	.23	.25	— .02
3.0	2.2	.22	.30	— .08
3.0	2.5	.25	.30	— .05
3.5	3.0	.30	35	— .05
3.5	3.2	.32	.35	— .03
4.0	4.0	.40	.40	± .00
4.0	3.7	.37	.40	— .03
			Mean	— .027

chloride and potassium permanganate the second series of determinations was made with diluted portions of the solution of potassium permanganate instead of the solution of manganous chloride. (See Table 2). These portions were treated like those reported in Table 1 and were then compared with standards prepared from the same solution of potassium permanganate. The average amount found was 0.027 milligram less than actually present although the differences were variable. When 0.00 to 0.10 milligram of manganese is present the error is as great as 50 per cent. Though the error is only about 10 per cent when 0.3 or 0.4 milligram is present it is still a serious error. These results indicate that either the oxidation to permanganate is incomplete or there is some reduction in subsequent steps, as the color produced is not so deep as that produced by a standard solution of potassium permanganate diluted to an equivalent content of manganese.

A third series of determinations (Table 3) was, therefore, made in which the standards for comparison were made from the solution of manganous sulphate treated in the same manner as the samples

TABLE 3.—THIRD SERIES OF DETERMINATIONS OF MANGANESE BY THE LEAD-PEROXIDE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN DISTILLED WATER COMPARED WITH DILUTE STANDARD SOLUTION OF MANGANOUS SULPHATE TREATED IN THE SAME MANNER.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard manganous sulphate.	Determined content.	Theoretical content.	Excess of determined over theoretical value.
0.0	0.0	0.00	0.00	±0.00
.2	.0	.00	.025	— .025
.2	.0	.00	.025	— .025
.4	.6	.06	.050	+ .01
.4	.4	.04	.050	— .01
.6	.8	.08	.075	+ .005
.6	.4	.04	.075	— .035
.8	1.2	.12	.100	+ .02
.8	1.5	.15	.100	+ .05
1.0	1.1	.11	.125	— .015
1.0	1.2	.12	.125	— .005
1.2	1.0	.10	.150	— .05
1.2	1.1	.16	.150	+ .01
1.5	2.3	.28	.187	+ .043
1.5	2.0	.20	.187	+ .013
2.0	1.8	.18	.250	— .07
2.0	1.9	.28	.250	+ .03
2.5	3.0	.30	.312	— .012
2.5	3.2	.32	.312	+ .008
3.0	4.0	.40	.375	+ .025
3.0	4.0	.40	.375	+ .025
3.5	3.5	.35	.438	— .088
3.5	4.0	.40	.438	— .038
4.0	5.0	.50	.500	± .000
4.0	6.0	.60	.500	+ .100
			Mean	— .001

were treated on the supposition that standards thus prepared should be exactly comparable with the sample. The results obtained were, however, very erratic, some being too high and some too low. Even when carried out under conditions which were as nearly similar as possible checks could not be obtained, and the error was as great as 30 per cent in many tests.

TABLE 4.—FOURTH SERIES OF DETERMINATIONS OF MANGANESE BY THE LEAD-PEROXIDE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN DISTILLED WATER COMPARED WITH DILUTE STANDARD SOLUTION OF MANGANOUS SULPHATE TREATED IN THE SAME MANNER AND DECANTED INTO NESSLER TUBES.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard manganous sulphate.	Determined content.	Theoretical content.	Excess of determined over theoretical value.
0.0	0.0	0.00	0.00	±0.00
.2	.2	.02	.025	— .005
.2	.2	.02	.025	— .005
.4	.5	.05	.050	± .00
.4	6	.06	.050	+ .01
.6	.7	.07	.075	— .005
.6	.8	.08	.075	+ .005
.8	1.2	.12	.100	+ .02
.8	1.0	.10	.100	± .00
1.0	1.2	.12	.125	— .005
1.0	1.0	.10	.125	— .025
1.2	1.4	.14	.150	— .01
1.2	1.7	.17	.150	+ .02
1.5	2.0	.20	.187	+ .013
1.5	2.2	.22	.187	+ .033
2.0	2.5	.25	.250	± .00
2.0	2.0	.20	.250	— .05
2.5	3.5	.35	.312	+ .038
2.5	3.0	.30	312	— .012
3.0	4.0	.40	.375	+ .025
3.0	4.5	.45	.375	+ .075
3.5	5.0	.50	.438	+ .062
3.5	4.5	.45	.438	+ .012
4.0	5.0	.50	.500	± .000
4.0	6.0	.60	.500	+ .100
			Mean	+ .012

The most probable source of error in the determination seemed to be in filtering through asbestos, as a very small amount of a reducing agent, like organic matter or compounds of manganese in the filter medium, would easily affect such very dilute solutions of permanganate. In order to eliminate this factor the determinations were made without filtration. Series 4 (Table 4) was made with manganous chloride diluted with distilled water. The comparisons were made, after the treated solutions had been decanted into Nessler tubes, with standard solutions of manganous sulfate treated in all respects like the samples. Series 5 (Table 5) was like series 4 except that the comparison of the solutions was made in the original beak-

ers after allowing the lead peroxide to settle. Series 6 (Table 6) was like series 5 except that the samples were prepared by adding the solution of manganous chloride to tap water instead of distilled water. The tap water is a bicarbonate water from deep wells; it contains no manganese and practically no chloride or sulphate; it has a turbidity of 5 parts, a color of 15 parts, due to its content of iron and organic matter, and a content of iron of 2 parts per million. The results of these three series show much greater accuracy than those of the first three, in which the solutions were filtered through asbestos. In series 4, in which the comparisons were made after the supernatant liquid had been decanted into Nessler tubes, difficulty was experienced on account of incomplete settling of the lead peroxide, some was invariably decanted, thus causing a dark color, which obscured the color to be compared. In series 5, in which comparisons were made in the original beakers, this difficulty was not encountered. The colors can not be matched so accurately in beakers, however, as the relatively shallow depths of solution make the differences in color appear less marked. The determinations made with tap water in

TABLE 5.—FIFTH SERIES OF DETERMINATIONS OF MANGANESE BY THE LEAD-PEROXIDE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN DISTILLED WATER COMPARED WITH DILUTE STANDARD SOLUTION OF MANGANOUS SULPHATE TREATED IN THE SAME MANNER IN ORIGINAL BEAKERS.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard manganous sulphate.	Determined content.	Theoretical content.	Excess of determined over theoretical value.
0.0	0.00	0.00	0.00	±0.00
.2	.2	.02	.025	— .005
.2	.2	.02	.025	— .005
.4	.5	.05	.050	± .00
.4	.4	.04	.050	— .01
.6	.7	.07	.075	— .005
.6	.6	.06	.075	— .015
.8	1.2	.12	.100	+ .02
.8	1.0	.10	.100	± .00
1.0	1.4	.14	.125	+ .015
1.0	1.1	.11	.125	— .015
1.2	1.5	.15	.150	± .00
1.2	1.4	.14	.150	— .01
1.5	2.0	.20	.187	+ .013
1.5	1.6	.16	.187	— .027
2.0	2.5	.25	.250	± .00
2.0	3.0	.25	.250	± .00
2.5	3.5	.35	.312	+ .038
2.5	3.0	.30	.312	— .012
3.0	4.0	.40	.375	+ .025
3.0	3.5	.35	.375	— .025
3.5	4.5	.45	.438	+ .012
3.5	4.0	.40	.438	— .038
4.0	5.0	.50	.500	± .000
4.0	5.0	.50	.500	± .000
			Mean	— .002

series 6 are as accurate as those with distilled water. Manganese can, therefore, be determined with a fair degree of accuracy by the lead-peroxide method in waters which contain little chloride and organic matter. A content as small as 0.02 milligram can be detected in a volume of 50 cubic centimeters by comparison of colors in Nessler tubes. The presence of organic matter in large amounts causes error, but the error from this source in ordinary samples is inappreciable as the results with tap water show.

The presence of chloride, which has a reducing action on permanganate, also causes an error. In order to determine how serious the effect due to chloride might be, series 7 (Table 7) was conducted, in which evaporation with sulphuric acid was omitted and 5 milligrams of chloride as sodium chloride was added to tap water. Low results were generally obtained. The average deviation from the theoretical values is .015 milligram. When 10 and 25 milligrams of chloride were present no test whatever for manganese could be obtained. It is essential, therefore, that chloride be removed for serious errors are introduced even by the presence of small amounts

TABLE 6.—SIXTH SERIES OF DETERMINATIONS OF MANGANESE BY THE LEAD-PEROXIDE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN TAP WATER COMPARED WITH DILUTE STANDARD SOLUTION OF MANGANOUS SULPHATE TREATED IN THE SAME MANNER IN ORIGINAL BEAKERS.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard manganous sulphate.	Determined content.	Theoretical content.	Excess of determined over theoretical value.
0.0	0.0	0.00	0.00	±0.00
.2	.2	.02	.025	— .005
.2	.2	.02	.025	— .005
.4	.5	.05	.050	± .00
.4	.5	.06	.050	+ .01
.6	.7	.07	.075	— .005
.6	.8	.08	.075	+ .005
.8	1.0	.10	.100	± .00
.8	1.0	.10	.100	± .00
1.0	1.2	.12	.125	— .005
1.0	1.4	.14	.125	+ .015
1.2	1.5	.15	.150	± .00
1.2	1.7	.17	.150	+ .02
1.5	2.0	.20	.187	+ .013
1.5	1.7	.17	.187	— .017
2.0	2.0	.20	.250	— .05
2.0	2.3	.23	.250	— .02
2.5	3.0	.30	.312	— .012
2.5	3.5	.35	.312	+ .038
3.0	3.5	.35	.375	— .025
3.0	4.0	.40	.375	+ .025
3.5	4.0	.40	.438	— .038
3.5	4.0	.40	.438	— .038
4.0	5.0	.50	.500	± .000
4.0	5.0	.50	.500	± .000
			Mean	— .004

of that radicle. Chloride is present in many natural waters in amounts greater than those used in these experiments.

THE SODIUM-BISMUTHATE METHOD

Schneider[1] appears to have been the first to use bismuth peroxide for the oxidation of manganous salts to permanganate. Other workers found, however, that the presence of chloride in this oxide was deleterious, and to overcome this trouble Reddrop and Ramage[2] substituted sodium bismuthate, which could be more easily obtained free from chloride. The bismuthate method has been used widely in analysis of iron and steel and has been shown to be accurate. It is described by Dufty,[3] Blair,[4] Blum,[5] Hillebrand and Blum,[6] and others. Weston[7] first advocated it for use in water analysis in 1907,

TABLE 7.—SEVENTH SERIES OF DETERMINATIONS OF MANGANESE BY THE LEAD-PEROXIDE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN TAP WATER COMPARED WITH DILUTE STANDARD SOLUTION OF MANGANOUS SULPHATE IN THE PRESENCE OF 5 MILLIGRAMS OF CHLORIDE.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard manganous sulphate.	Determined content.	Theoretical content.	Excess of determined over theoretical value.
0.0	0.0	0.00	0.00	±0.00
.2	.2	.02	.025	— .005
.2	.2	.02	.025	— .005
.4	.3	.03	.050	— .02
.4	.4	.03	.050	— .02
.6	.5	.05	.075	— .025
.6	.6	.06	.075	— .015
.8	.7	.07	.100	— .03
.8	.9	.09	.100	— .01
1.0	1.1	.11	.125	— .015
1.0	1.2	.12	.125	— .005
1.2	1.2	.12	.150	— .03
1.2	1.4	.14	.150	— .01
1.5	1.8	.18	.187	— .007
1.5	2.0	.20	.187	+ .013
2.0	2.5	.25	.250	± .000
2.0	2.0	.20	.250	— .05
2.5	3.0	.30	.312	— .012
2.5	3.0	.30	.312	— .012
3.0	3.5	.35	.375	— .025
3.0	3.5	.35	.375	— .025
			Mean.....	— .015

[1]Schneider, L., Methode zur Bestimmung von Mangan: Dingl. poly. J. 269, 224 (1888).

[2]Reddrop, Joseph, and Ramage, Hugh, Volumetric estimation of manganese: J. Chem. Soc., 67, 268-77 (1895).

[3]Dufty, Lawrence, Volumetric estimation of manganese: Chem. News, 84, 248 (1901).

[4]Blair, A. A., The bismuthate method for the determination of manganese: J. Am. Chem. Soc., 26, 793-801 (1904).

[5]Blum, William, Determination of manganese as sulphate and by the sodium-bismuthate method: Orig. Com. 8th Intern. Congr. Appl. Chem., 1, 61-85 (1912).

[6]Hillebrand, W. F., and Blum, William, The determination of manganese by the sodium-bismuthate method: J. Ind. Eng. Chem., 3, 374-6 (1911).

[7]Weston, R. S., The determination of manganese in water: J. Am. Chem. Soc., 29, 1074-8 (1907).

before which year manganese in water was seldom determined. He describes the method, giving some data which show it to be sufficiently accurate. The procedure for this method recommended by the committee on standard methods of water analysis[1] in the edition published in 1912 is based on Weston's work.

The procedure used in this investigation is essentially as follows. Different amounts of the standard solution of manganous chloride were diluted with distilled water and with tap water. Each portion was then evaporated with one or two drops of sulphuric acid (1 to 3) until white fumes appeared. Distilled water, dilute nitric acid, and 0.5 gram of sodium bismuthate were then added, after which the solution was heated until the pink color disappeared. After it had cooled somewhat an excess of sodium bismuthate was added, the solution was thoroughly stirred, then filtered through an asbestos mat in a Gooch crucible, which had been washed, ignited, and treated with potassium permanganate. The solution was then transferred to a Nessler tube and compared with two sets of standards, one prepared

TABLE 8.—FIRST SERIES OF DETERMINATIONS OF MANGANESE BY THE BISMUTHATE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN DISTILLED WATER COMPARED WITH DILUTE STANDARD SOLUTION OF POTASSIUM PERMANGANATE.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard permanganate.	Determined content.	Theoretical content.	Excess of determined over theoretical content.
0.0	0.0	0.00	0.00	±0.00
.2	.2	.02	.025	— .005
.2	.2	.02	.025	— .005
.4	.4	.04	.050	— .01
.4	.5	.05	.050	± .00
.6	.7	.07	.075	— .005
.6	.7	.07	.075	— .005
.8	1.0	.10	.100	± .00
.8	1.0	.10	.100	± .00
1.0	1.2	.12	.125	— .005
1.0	1.2	.12	.125	— .005
1.2	1.5	.15	.150	± .00
1.2	1.4	.14	.150	— .01
1.5	2.0	.20	.187	+ .013
1.5	1.7	.17	.187	— .017
2.0	2.5	.25	.250	± .00
2.0	2.2	.22	.250	— .03
2.5	3.0	.30	.312	— .012
2.5	3.2	.32	.312	+ .008
3.0	3.5	.35	.375	— .025
3.0	4.0	.40	.375	+ .025
3.5	4.5	.45	.438	+ .012
3.5	4.5	.45	.438	+ .012
4.0	5.0	.50	.500	± .000
4.0	5.0	.50	.500	± .000
			Mean	— .003

[1]Standard methods for the examination of water and sewage, Am. Pub. Health Assoc., New York, 2nd ed., 49-51 (1912).

by diluting standard potassium permanganate and the other by treating standard solutions of manganous sulphate like the samples. The results obtained are shown in Tables 8 and 9. A third series (Table 10) was run in the same manner except that tap water was used instead of distilled water. Filtration through asbestos does not seem to have any appreciable reducing effect on the permanganate when sodium bismuthate is used as the oxidizing agent. This seems strange for when lead peroxide was used the effect was so great as to cause uniformly low values. The results indicate that the bismuthate method is accurate under all the conditions here observed. A content of 0.01 milligram of manganese in a volume of 50 cubic centimeters can be detected by comparison in Nessler tubes.

In order to determine how seriously the results are affected by the presence of chloride 5, 10, and 25 milligrams of chloride as sodium chloride were added to different portions, and evaporation with sulfuric acid was omitted. The determinations made under these conditions are shown in Table 11. The results indicate that chloride has no appreciable effect in amounts of 5 milligrams or less.

TABLE 9.—SECOND SERIES OF DETERMINATIONS OF MANGANESE BY THE BISMUTHATE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN DISTILLED WATER COMPARED WITH DILUTE STANDARD SOLUTION OF MANGANOUS SULPHATE TREATED IN THE SAME MANNER.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard manganous sulphate.	Determined content.	Theoretical content.	Excess of determined over theoretical content.
0.0	0.0	0.00	0.00	±0.00
.2	.2	.02	.025	— .005
.2	.2	.02	.025	— .005
.4	.4	.04	.050	— .01
.4	.5	.05	.050	± .00
.6	.7	.07	.075	— .005
.6	.8	.08	.075	+ .005
.8	1.0	.10	.100	± .00
.8	1.0	.10	.100	± .00
1.0	1.2	.12	.125	— .005
1.0	1.1	.11	.125	— .015
1.2	1.5	.15	.150	± .00
1.2	1.4	.14	.150	— .01
1.5	2.0	.20	.187	+ .013
1.5	2.0	.20	.187	+ .013
2.0	2.5	.25	.250	± .00
2.0	2.5	.28	.250	+ .03
2.5	3.0	.30	.312	— .012
2.5	3.5	.35	.312	+ .038
3.0	3.5	.35	.375	— .025
3.0	4.0	.40	.375	+ .025
3.5	4.5	.45	.438	+ .012
3.5	4.0	.40	.438	— .038
4.0	5.0	.50	.500	± .000
4.0	5.0	.50	.500	± .000
			Mean	+ .0002

When 10 milligrams or more of chloride are present the results are low. The effect of chloride in the bismuthate method is much less pronounced than in the peroxide method, in which the presence of more than 10 milligrams of chloride wholly prevented the appearance of the color of permanganate.

The bismuthate method is decidedly superior to the lead-peroxide method. The color of the permanganate is not appreciably weakened by filtration through asbestos. Comparison of colors may, therefore, be made by filtering and transferring to Nessler tubes. The presence of chloride does not interfere so seriously in the bismuthate as in the lead-peroxide method. That the permanganate is not so easily reducible in the presence of sodium bismuthate as in the presence of lead peroxide is probably due to the fact that the bismuthate is a more active oxidizing agent than the peroxide. The results were as accurate when the colors were compared with those of dilute standard solutions of potassium permanganate as when compared with those of solutions of manganous sulphate treated like the samples. The

TABLE 10.—THIRD SERIES OF DETERMINATIONS OF MANGANESE BY THE BISMUTHATE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN TAP WATER COMPARED WITH DILUTE STANDARD SOLUTION OF MANGANOUS SULPHATE TREATED IN THE SAME MANNER.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard manganous sulphate.	Determined content.	Theoretical content.	Excess of determined over theoretical content.
0.0	0.0	0.00	0.00	±0.00
.2	.2	.02	.025	— .005
.2	.3	.03	.025	+ .005
.4	.5	.05	.050	± .00
.4	.5	.05	.050	± .00
.6	.8	.08	.075	+ .005
.6	.7	.07	.075	— .005
.8	.10	.10	.100	± .00
.8	.08	.08	.100	— .02
1.0	.12	.12	.125	— .005
1.0	.11	.11	.125	+ .015
1.2	.15	.15	.150	± .00
1.2	.15	.15	.150	± .00
1.5	2.0	.20	.187	+ .013
1.5	1.8	.18	.187	— .007
2.0	2.5	.25	.250	± .00
2.0	2.2	.22	.250	— .03
2.5	3.0	.30	.312	— .012
2.5	3.5	.35	.312	+ .038
3.0	4.0	.40	.375	+ .025
3.0	4.0	.40	.375	+ .025
3.5	4.5	.45	.438	+ .012
3.5	4.0	.40	.438	— .038
4.0	5.0	.50	.500	± .000
4.0	5.0	.50	.500	± .000
			Mean	+ .001

use of sodium bismuthate permits detection of a slightly smaller amount of manganese than the use of lead peroxide.

THE PERSULPHATE METHOD

The fact that persulphate oxidizes manganous salts to permanganate in the presence of silver nitrate was discovered by Marshall[1], who suggested the reaction as a qualitative test for manganese. Walters[2] first used a modified form of the method for the quantitative determination of manganese in iron and steel. After the manganese had been oxidized to permanganate the amount was found by titrating with arsenious acid. This method is now widely used in metallurgical work.

In water analysis comparison of the colors of the solutions of permanganate is usually made instead of a titration. The persulphate

TABLE 11.—FOURTH SERIES OF DETERMINATIONS OF MANGANESE BY THE BISMUTHATE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN DISTILLED WATER CONTAINING CHLORIDE COMPARED WITH DILUTE STANDARD SOLUTION OF POTASSIUM PERMANGANATE.

[Results expressed in milligrams of manganese.]

Solution of manganous chloride.	Theoretical content.	Determined content of manganese in presence of designated amounts of chloride.			
		5 mg.	10 mg.	25 mg.	50 mg.
Cubic centimeters					
0.0	0.000	0.00	0.00	0.00	0.00
.2	.025	.02	.02	.00	.00
.2	.025	.03	.02	.00	.00
.4	.050	.05	.04	.03	.00
.4	.050	.05	.03	.02	.00
.6	.075	.08	.07	.05	.03
.6	.075	.07	.08	.06	.04
.8	.100	.10	.09	.08	.05
.8	.100	.10	.10	.07	.05
1.0	.125	.12	.12	.10	.08
1.0	.125	.14	.12	.08	.10
1.2	.150	.15	.14	.14	.12
1.2	.150	.15	.13	.12	.10
1.5	.187	.20	.17	.15	.12
1.5	.187	.20	.15	.15	.15
2.0	.250	.25	.20	.20	.12
2.0	.250	.30	.25	.20	.20
2.5	.312	.30	.30	.25	.25
2.5	.312	.28	.32	.28	.20
3.0	.375	.35	.32	.30	.30
3.0	.375	.40	.32	.32	.25
3.5	.438	.45	.40	.40	.20
3.5	.438	.45	.35	.30	.20
4.0	.504	.50	.45	.37	.25
4.0	.504	.40	.45	.40	.20

[1]Marshall, Hugh, The detection and estimation of minute quantites of manganese: Chem. News, 83, 76 (1901).

[2]Walters, H. E., Ammonium persulphate as a substitute for lead peroxide in the colorimetric estimation of manganese: Chem. News, 84, 239-40 (1901).

method has been advocated by Lührig and Becker,[1] Rodenburg,[2] Haas,[3] Schowalter,[4] Hartwig and Schellbach,[5] and Tillmans and Mildner[6], but most of these authors present no data as to the accuracy of the method.

In the writer's work with the ammonium-persulphate method different amounts of the standard solution of manganous chloride were diluted with distilled water or with tap water to about 50 cubic centimeters each. Two cubic centimeters of nitric acid (1 to 1) and 5 cubic centimeters of 2.0 per cent solution of silver nitrate were added. After the mixture had been boiled and shaken it was filtered. About 0.5 gram of crystals of ammonium persulphate was added to the filtrate, and the solution was heated gently on the hot plate until the maximum color of permanganate had developed after which it was transferred to a 50 cubic centimeter Nessler tube. The color was compared with those of standards prepared by diluting with water a standard solution of potassium permanganate or by treating diluted amounts of a standard solution of manganous sulphate with nitric acid, silver nitrate, and ammonium persulphate like the sample. The

TABLE 12.—FIRST SERIES OF DETERMINATIONS OF MANGANESE BY THE PERSULPHATE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN DISTILLED WATER COMPARED WITH DILUTE STANDARD SOLUTION OF POTASSIUM PERMANGANATE.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard permanganate.	Determined content.	Theoretical content.	Excess of determined over theoretical content.
0.0	0.0	0.00	0.00	±0.00
.2	.2	.02	.025	— .005
.2	.3	.03	.025	+ .005
.4	.4	.04	.050	— .01
.4	.5	.05	.050	± .00
.6	.7	.07	.075	— .005
.6	.7	.07	.075	— .005
.8	1.0	.10	.100	± .00
.8	1.1	.11	.100	+ .01
1.0	1.2	.12	.125	— .005
1.0	1.0	.10	.125	— .025
			Mean	— .003

[1]Lührig, H., and Becker, W., Zur Bestimmung des Mangans im Trinkwasser: Pharm. Zentralhalle, 48, 137-42 (1907).

[2]Rodenburg, J., Over mangaanbepaling in leidingwater: Chem. Weekblad, 7, 877-9 (1910).

[3]Haas, Fritz, Ueber die colorimetrische Bestimmung kleiner Mengen von Mangan im Trinkwasser: Z. Nahr. Genussm., 25, 392-5 (1913).

[4]Schowalter, E., Colorimetrische Bestimmung kleiner Mengen von Mangan im Trinkwasser: Z. Nahr. Genussm., 26, 104-8 (1913); also Studien zur Kenntnis des Verlaufs der Marshall'schen Manganreaktion: 27, 553-62 (1914).

[5]Hartwig, L., and Schellbach, H., Colorimetrische Bestimmung von kleinen Mengen Mangan in Trinkwasser: Z. Nahr. Genussm., 26, 439-42 (1913).

[6]Tillmans, J., and Mildner, H., Mangan im Wasser, sein Nachweis und seine Bestimmung: J. Gasbel., 57, 496-501, 523-6, 544-7 (1914).

results obtained by comparison of colors according to these methods are given in Tables 12, 13, 14, and 15.

In the comparisons with standard solution of potassium permanganate diluted with water (Table 12) amounts of manganese greater than 0.125 milligram could not be compared easily on account of the difference in shade between the standards of permanganate and the samples. The solutions of potassium permanganate were reddish purple while the samples were bluish purple. This difference in hue was noticeable in all the concentrations used, but it did not cause great trouble except when the manganese is present in amounts greater than 0.10 or 0.12 milligram. With lower concentrations accurate results were obtained, but with higher concentrations the comparison was too unsatisfactory to be used.

When the standards were prepared by treating diluted solutions of manganous sulphate in the same manner as the samples, no difficulty was experienced in making the comparisons, and the results (Tables 13 and 14) show that the method is accurate. Series 3 in which the solution of manganous chloride was diluted with tap water

TABLE 13.—SECOND SERIES OF DETERMINATIONS OF MANGANESE BY THE PERSULPHATE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN DISTILLED WATER COMPARED WITH DILUTE STANDARD SOLUTION OF MANGANOUS SULPHATE TREATED IN THE SAME MANNER.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard manganous sulphate.	Determined content.	Theoretical content.	Excess of determined over theoretical content.
0.0	0.0	0.00	0.00	±0.00
.2	.2	.02	.025	— .005
.2	.25	.025	.025	± .00
.4	.6	.06	.050	∓ .01
.4	.5	.05	.050	± .00
.6	.7	.07	.075	— .005
.6	.8	.08	.075	+ .005
.8	1.0	.10	.100	± .00
.8	1.1	.11	.100	∓ .01
1.0	1.2	.12	.125	— .005
1.0	1.2	.12	.125	— .005
1.2	1.4	.14	.150	— .01
1.2	1.4	.16	.150	+ .01
1.5	1.8	.18	.187	— .007
1.5	1.8	.18	.187	— .007
2.0	2.4	.24	.250	— .01
2.0	2.5	.25	.250	± .00
2.5	3.0	.30	.312	— .012
2.5	3.3	.33	.312	+ .018
3.0	3.5	.35	.375	— .025
3.0	3.8	.38	.375	+ .005
3.5	4.0	.40	.438	— .038
3.5	4.5	.45	.438	+ .012
4.0	5.0	.50	.500	± .000
4.0	4.5	.45	.500	— .050
			Mean	— .004

gave as accurate results as those in which distilled water was used, the mean differences for the two series of twenty-five determinations each being, respectively,—0.003 milligram and—0.004 milligram. The results show the desirability of using standards which have been oxidized with persulphate and treated in all respects like the samples. A content of 0.005 milligram of manganese in a volume of 50 cubic centimeters was easily detected under the conditions of the test.

Lührig[1] states that a high content of chloride interferes in the persulphate method by causing a blue coloration, and that iron interferes by causing a reddish coloration. Yet accurate results were obtained by the writer in a series of determinations in which 50, 100, and 200 milligrams of chloride as sodium chloride were present. (See Table 15.) No bluish coloration was noted, and no difficulty was experienced in matching the colors. A large excess of silver nitrate and ammonium persulphate should be avoided as it seems to produce a cloudiness perhaps by precipitate of silver peroxide. Mar-

TABLE 14.—THIRD SERIES OF DETERMINATIONS OF MANGANESE BY THE PERSULPHATE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN TAP WATER COMPARED WITH DILUTE STANDARD SOLUTION OF MANGANOUS SULPHATE TREATED IN THE SAME MANNER.

Cubic centimeters of solution.		Milligrams of manganese.		
Manganous chloride.	Standard manganous sulphate.	Determined content.	Theoretical content.	Excess of determined over theoretical content.
0.0	0.0	0.00	0.00	±0.00
.2	.8	.03	.025	+ .005
.2	.2	.02	.025	— .005
.4	.5	.05	.050	± .00
.4	.5	.05	.050	± .00
.6	.7	.07	.075	— .005
.6	.7	.07	.075	— .005
.8	.9	.09	.100	— .010
.8	1.0	.10	.100	± .000
1.0	1.2	.12	.125	— .005
1.0	1.1	.11	.125	— .015
1.2	1.4	.14	.150	— .01
1.2	1.5	.15	.150	± .00
1.5	1.8	.18	.187	— .007
1.5	1.9	.19	.187	+ .003
2.0	2.5	.25	.250	± .00
2.0	2.4	.24	.250	— .01
2.5	3.2	.32	.312	+ .008
2.5	3.3	.33	.312	+ .018
3.0	3.5	.35	.375	— .025
3.0	3.8	.38	.375	+ .005
3.5	4.5	.45	.438	+ .012
3.5	4.5	.45	.438	+ .012
4.0	5.0	.50	.500	± .000
4.0	4.7	.47	.500	— .030
			Mean	— .003

[1]Lührig, H., Die colorimetrische Bestimmung kleiner Manganmengen im Wasser: Chem. Ztg., 38, 781-3 (1914).

shall[1] prepared silver peroxide by this method, and the interference noted by Lührig is probably caused thus. Large amounts of iron doubtless interfere on account of the yellow color of ferric salts. When manganese is present the mixture produces the reddish coloration noted by Lührig.

COMPARISON OF THREE COLORIMETRIC METHODS

In order to compare the three colorimetric methods for determination of manganese under working conditions, the manganese in several natural waters was determined by each method. The amounts found, together with the amounts of residue, chloride, iron, and the alkalinity to show the character of the waters, are given in Table 16. The samples were taken below Streator from Vermilion River, which is polluted by coal-mine drainage, and their contents of iron and chloride are large. In the persulphate method chloride was precipitated by silver nitrate, added in slight excess, and was removed by filtration. The colorimetric comparison was made with standard

TABLE 15.—FOURTH SERIES OF DETERMINATIONS OF MANGANESE BY THE PERSULPHATE METHOD.

SOLUTIONS OF KNOWN CONTENT OF MANGANOUS CHLORIDE IN TAP WATER CONTAINING CHLORIDE COMPARED WITH STANDARD SOLUTION OF MANGANOUS SULPHATE TREATED IN THE SAME MANNER.

[Results expressed in milligrams of manganese.]

Solution of manganous chloride.	Theoretical content.	Determined content of manganese in presence of designated amounts of chloride.		
		50 mg.	100 mg.	200 mg.
Cubic centimeters.				
0.0	0.000	0.000	0.000	0.000
.2	.025	.02	.02	.02
.2	.025	.02	.02	.02
.4	.050	.04	.05	.04
.4	.050	.05	.05	.05
.6	.075	.07	.07	.08
.6	.075	.08	.07	.08
.8	.100	.11	.09	.10
.8	.100	.10	.10	.10
1.0	.125	.12	.13	.12
1.0	.125	.12	.12	.12
1.2	.150	.14	.15	.16
1.2	.150	.16	.16	.15
1.5	.180	.18	.19	.17
1.5	.180	.20	.20	.19
2.0	.250	.22	.22	.25
2.0	.250	.25	.24	.25
2.5	.312	.30	.30	.32
2.5	.312	.28	.30	.30
3.0	.375	.35	.35	.40
3.0	.375	.40	.35	.40
3.5	.438	.45	.40	.45
3.5	.438	.45	.45	.50
4.0	.504	.50	.45	.55
4.0	.504	.50	.50	.50

[1]Marshall, Hugh, The action of silver salts on solution of ammonium persulphate: Proc. Royal Soc. Edinburgh, 23, 163-8 (1900).

solution of manganous sulphate treated in the same manner as the sample. In the bismuthate method evaporation of the sample with sulphuric acid was omitted, and the colorimetric comparison was made with standards prepared by diluting the standard solution of potassium permanganate. In the lead-peroxide method the tests were made with and without filtration through Gooch crucibles and with and without evaporation with sulphuric acid, and standards were prepared by treating portions of the dilute solution of manganous sulfate in the same manner as the samples. The amounts determined by the persulphate and the bismuthate methods agree very well. The amounts found by the lead-peroxide method with chloride removed and without filtering through Gooch crucibles also agree very well with those obtained in the persulphate and the bismuthate methods. The results were low, however, when chloride was not first removed and irregular results were obtained when the Gooch crucible was used for filtration.

TABLE 16.—DETERMINATIONS OF MANGANESE IN NATURAL WATERS BY COLORIMETRIC METHODS.

[Parts per million.]

Total residue.	Chloride (Cl).	Alkalinity as Ca CO_3.	Iron (Fe).	Manganese (Mn).					
				Persulphate method.	Bismuthate method.	Lead-peroxide method.			
						Gooch crucible.		Decantation.	
						Chlorine not removed.	Chlorine removed.	Chlorine not removed.	Chlorine removed.
848	42	460	0.4	0.25	0.15	0.0	0.0	0.2	0.2
2328	60	20	150.	4.5	4.0	3.0	3.0	4.0	5.0
2070	80	20	86.	4.0	3.2	2.0	4.8	3.0	4.0
2290	83	26	90.	4.0	4.2	2.5	3.2	3.0	4.0
2198	84	40	65.	5.5	5.0	3.0	5.0	5.0	5.0
2371	103	60	66.	7.5	7.0	6.0	7.0	7.0	8.0
2293	103	122	4.0	8.0	9.5	4.0	6.0	6.0	8.0
345	25	144	.2	.0	.0	.0	..	.0	..
2396	102	90	46.5	9.0	8.5	6.0	7.0	8.0	7.0
1591	17	92	126.5	1.4	1.4	0.6	1.6	1.0	1.5
2660	65	200	57.5	2.0	1.8	1.8	2.0	2.0	2.0
1970	92	4	48.0	4.0	4.0	2.0	6.0	3.0	4.0

RELATIVE VALUE OF COLORIMETRIC METHODS

The persulphate method is the most convenient and accurate method for the colorimetric determination of manganese in water. Chloride, being necessarily removed by precipitation, does not interfere. As small amount as 0.005 milligram of manganese in a volume of 50 cubic centimeters, equivalent to 0.1 part per million, can be detected. The bismuthate method recommended by the committee on

standard methods of water analysis[1] is accurate and reliable. The presence of chloride in amounts less than 5 milligrams does not interfere with this determination, and evaporation with sulphuric acid may be omitted unless the water contains much organic matter. By this method 0.01 milligram of manganese in a volume of 50 cubic centimeters, equivalent to 0.2 part per million, can be detected. The lead-peroxide method accepted by the committee on standard methods of water analysis gives results which are seriously low because of reduction of permanganate in using the Gooch crucible. If this step is omitted more nearly accurate results are obtained. The presence of chloride interferes in this method more seriously than in either of the others, and if more than 5 milligrams of chloride are present no manganese may be found even if a comparatively large amount is present; evaporation with sulphuric acid is, therefore, necessary. About 0.02 milligram of manganese in a volume of 50 cubic centimeters, equivalent to 0.4 part per million, can be detected by the decantation method. The peroxide method is at best the least sensitive of the three, and it should be rejected as a standard method.

It seems advisable to adopt as standard:

(1) The persulphate method, in which colorless nitric acid should be used, evaporation with sulphuric acid should be omitted unless large amounts of organic matter are present, and comparison should be made with standards prepared by treating solutions of manganous sulphate exactly like the sample;

(2) The bismuthate method, in which colorless nitric acid should be used, evaporation with sulphuric acid should be omitted unless more than 5 milligrams of chloride or much organic matter is present, and comparison should be made with standards prepared by treating standard solutions of manganous sulphate exactly like the sample or by diluting a freshly prepared solution of potassium permanganate.

MANGANESE IN WATER SUPPLIES

General occurrence

The presence of manganese in water supplies in concentrations great enough to be significant has always been considered rather unusual, particularly in the United States. Manganese has been encountered in several water supplies in Europe.

[1]Standard methods for the examination of water and sewage, Am. Pub. Health Assoc., New York, 2nd ed., 49-51 (1912).

R. S. Weston[1] cites some twenty ground-water supplies in this country and in Europe which have been reported to contain manganese.

TABLE 17.—MANGANESE IN CERTAIN MUNICIPAL WATER SUPPLIES.

	Parts per million.
Arad, Hungary	Present
Babylon, N. Y.	.07
Bayshore, N. Y.	.37
Berlin, Germany	Present
Björnstorp, Sweden	3.4 — 53.4
Brunswick, Germany	Present
Breslau, Germany	Trace— 110
Calverton, N. Y.	.30
Halle, Germany	1.50
Hamburg, Hofbrünnen	.45
Hanover, Germany	Present
Patchogue, N. Y.	.20
Reading, Mass.	.004— .56
Stargard, Germany	Present
Stettin, Germany	5.22
Superior, Wisconsin	.12
Shewsbury, Mass.	.10

The first water in this country in which manganese was reported in sufficient quantity to cause trouble was, from a well supplying a New England mill in 1898. This supply was abandoned because of its high content of manganese. Sixty-two springs in the United States are listed by Mason[2] as having been reported to contain manganese. He states that nearly half of them contain only traces of the element and that only seven contain as much as the 4.5 parts per million which he found in a mineral spring at Excelsior Springs, Mo. Raumer[3] reports a water near Fürth which contained 6.2 parts per million of manganese. Bailey[4] states that the well-water supply of Hutchinson, Kans., contains 1.0 part per million of manganese.

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[1]Weston, R. S., The purification of ground waters containing iron and manganese: Trans. Am. Soc. C. E., 64, 112-81 (1909).

[2]Mason, W. P., The manganese waters of Excelsior Springs: Chem. News, 61, 123 (1890).

[3]Raumer, E. von, Ueber das Auftreten von Eisen und Mangan in Wasserleitungswasser: Z. anal. Chem., 42, 590-602 (1903).

[4]Bailey, E. H. S., Occurrence of manganese in a deposit found in city water pipes: J. Am. Chem. Soc., 26, 714-5 (1904).

The trouble in Breslau[1] in 1906 is a classic example of injury to a water supply by very high contents of iron and manganese. Breslau was formerly supplied with water from Oder River, but in 1905 a supply was substituted from 313 driven wells 30 to 40 feet deep in Oder valley. In March, 1906, the Oder overflowed its banks, and soon afterward the turbidity, odor, hardness, residue, manganese, and iron in the ground-water supply enormously increased. The content of iron increased to 440 and the content of manganese to 220 parts per million. The filtered water from Oder River was necessarily substituted for the ground-water supply. Many explanations have been offered for this peculiar change in the quality of the water. Most authorities agree that it was caused by a process of oxidation and leaching of the soil, which contains a large amount of sulfides of iron and manganese. The iron sulfide was oxidized to iron sulfate by the dissolved oxygen of the river water. The water containing iron sulphate then percolated through the soil to the water-bearing strata, a part hydrolyzing to sulphuric acid which dissolved the manganese. Extensive experiments on the removal of iron and manganese from the supply have been carried on by a number of investigators.

Manganese waters at Björnstorp Estate, Sweden, are described by Weibull.[2] Pipes were clogged, and fabrics laundered in several waters from ponds and wells in the vicinity were turned yellow. Investigation showed that some of the waters contained as much as 6.3 parts per million of manganous oxide, or 5 parts per million of manganese which was precipitated upon exposure to the air. The rock formation in the vicinity is gneiss and diorite, the latter of which contains 8.2 per cent of manganous oxide, which probably accounts for the high content of manganese of the waters.

A study of the content of manganese of waters in France has been made by Jadin and Astrug.[3] In several city supplies 0.0005 to 0.015 part per million of manganese was found. Mineral waters at Vichy and Boulon contained 0.09 to 0.20 part per million. The content of manganese of sources very near each other widely differed.

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[1]Woy, Rudolph, Störung der Breslauer Wasserversorgung durch Mangansulfat: Z. öffent. Chem. 12, 121-125 (1906); Kritische Besprechung der Erfahrungen mit der Breslauer Grundwasserversorgung: 13, 401-411 (1907).

Lührig, H., Über die Ursachen der Breslauer Grundwasserverschlechterung und die Mittel zu ihrer Behelung: Z. Nahr. Genussm., 14, 40-63 (1907).

Beyschlag, F., and Michael R., Über die Grundwasserverhältnisse der Stadt Breslau: Z. prakt. Geol., 15, 153-64 (1907).

Lührig, H. and Blasky, A., Mangan in Grundwasser der Breslauer Wasserleitung und die Frage der Abscheidung des Mangansulfates aus demselben: Chem. Ztg., 31, 255-7 (1907).

Weston, R. S., The purification of ground waters containing iron and manganese: Trans. Am. Soc. C. E., 64, 112-81 (1909).

[2]Weibull, Mats, Ein manganhaltiges Wasser und eine Bildung von Braunstein bei Björnstorp in Sweden. Z. Nahr. Genussm., 14, 403-5 (1907).

[3]Jadin, F., and Astrug, A., Le manganèse dans les eaux d' alimentation et les eaux minerals: Compt. Rend., 157, 338-9 (1913).

Discovery of manganese in several city water supplies of Illinois prompted an investigation to determine what relations, if any, exist between geological formation and content of manganese and to determine the source of the manganese in the supplies. Accordingly, manganese, iron, and dissolved solids were determined in a large number of samples from representative sources throughout the State. Samples were taken from streams and from wells, concerning which reliable information was available concerning the geological strata penetrated. As complete information of this kind concerning many private wells is not available whereas rather complete logs are usually kept of city wells most of the supplies examined are city water supplies. The samples were taken at the original sources, preliminary work having shown that manganese may completely separate in the pipes before the water reaches distant taps.

Methods of Analysis

MANGANESE

The colorimetric persulfate method was used for the determination of manganese. Two hundred and fifty cubic centimeters of the sample were acidified with 2 cubic centimeters of nitric acid (1 to 1) and concentrated to a volume of less than 50 cubic centimeters. If the sample contained more than 0.20 milligram of manganese a smaller amount was used for the determination. Surface waters and in general waters showing a clayey or silica-like turbidity were filtered before making the determination. After concentration chloride was precipitated with a solution of silver nitrate added in slight excess, and the precipitate was removed by filtration. Samples which were very high in chloride were evaporated with sulphuric acid until white fumes were evolved, after which distilled water and a small amount of the solution of silver nitrate were added. One-half gram of crystals of ammonium persulphate was then added, and the solution was warmed until the maximum color of permanganate had developed. Standards were prepared containing 0.2, 0.4, 0.6, and more cubic centimeters of standard solution of manganous sulphate, which was diluted to similar volume and treated in exactly the same manner as the sample was treated. The sample and the standards were then transferred to 50-cubic centimeter Nessler tubes and the colors were compared. If the above procedure is followed the limit of detection is 0.02 part per million.

IRON

Iron was determined either colorimetrically with potassium sulphocyanide or by titration with permanganate after the weighed oxides of iron and aluminium had been fused and dissolved.

DISSOLVED SOLIDS

Dissolved solids is the residue obtained by evaporating to dryness 100 cubic centimeters of the sample, heating the residue at 180°C. for one hour, and weighing it. Samples having a clayey or silica-like turbidity were filtered before evaporation. If the turbidity was due to precipitated ferric hydroxide the sample was not filtered.

Manganese in Waters of Illinois

The supplies have been grouped as follows with reference to source:

1. Wells in Potsdam sandstone.
2. Wells in St. Peter sandstone.
3. Wells in limestone.
4. Wells in unconsolidated deposits.
5. Springs.
6. Coal-mine drainage.
7. Lakes and streams.

WELLS IN POTSDAM SANDSTONE

Seventeen supplies from wells entering Potsdam sandstone were examined. (See Table 18.) No manganese could be detected in fourteen of them. A small amount was found in three, 0.08 part per million in water from a well at Chicago, and 0.04 part in water from wells at Riverside and Utica. These amounts are so small as to be of little significance. The content of iron ranges from 0.0 to 3.6 parts per million and dissolved solids from 278 to 5,520 parts. No relation is apparent between the contents of manganese, iron, and total mineral matter. Manganese apparently is not present in most water from wells drawing chiefly from Potsdam sandstone in Illinois.

WELLS IN ST. PETER SANDSTONE

Twenty-eight samples from wells entering St. Peter sandstone were examined. (See Table 18.) Manganese was absent from all but two of them. One of these was from a 1,300-foot well at Elgin, which furnished a water containing 0.10 part per million. As this well is

TABLE 17.—CONTENT OF MANGANESE, IRON, AND DISSOLVED SOLIDS IN WATER FROM WELLS ENTERING POTSDAM SANDSTONE.

[Parts per million.]

Locality.	County.	Depth.	Manganese (Mn).	Iron (Fe).	Dissolved solids.
		Feet.			
Aledo	Mercer	3,165	0.00	0.0	2,078
Amboy	Lee	2,400	.00	1.4	450
Aurora	Kane	2,000	.00	.4	2,198
Belvidere	Boone	1,800	.00	.0	511
Blue Island	Cook	2,000	.00	.2	1,246
Byron	Ogle	2,000	.00	.0	288
Carbon Hill	Grundy	1,800	.00	.8	1,295
Chicago[a]	Cook	2,100	.08	3.6	5,520
Chicago[a]	do	1,600	.00	.4	1,057
Dixon[a]	Lee	1,922	.00	.1	301
East Dubuque	Jo Daviess	940	.00	.2	278
Forest Park	Cook	2,015	.00	.0	530
Minonk	Woodford	1,765	.00	.2	2,337
Morrison	Whiteside	2,048	.00	.5	293
Riverside	Cook	2,000	.04	.2	891
Utica	La Salle	350	.04	.5	444
Waukegan	Lake	1,300	.00	.1	557

[a]Not public supply.

TABLE 18.—CONTENT OF MANGANESE, IRON, AND DISSOLVED SOLIDS IN WATER FROM WELLS ENTERING ST. PETER SANDSTONE.

[Parts per million.]

Locality.	County.	Depth.	Manganese (Mn).	Iron (Fe).	Dissolved solids.
		Feet.			
Abingdon	Knox	1,350	0.00	0.0	1,323
Bellwood	Cook	1,400	.00	1.0	546
Chadwick	Carroll	600	.00	.3	399
Chenoa	McLean	2,100	.00	1.1	1,289
Cuba	Fulton	1,765	.00	.4	2,548
Elgin	Kane	1,300	.10	3.2	377
Do	do	1,300	.00	.4	493
Elmwood	Peoria	1,300	.00	.7	1,488
Farmington	Fulton	1,465	.00	.3	1,595
Galesburg	Knox	1,240	.00	.0	1,515
Genoa	DeKalb	1,500	.00	.0	315
Henry	Marshall	1,355	.00	.0	520
Ipava	Fulton	1,575	.00	.0	2,977
Jerseyville	Jersey	1,542	.00	.1	3,281
Kewanee	Henry	1,485	.00	.3	1,176
Lena	Stephenson	600	.00	.0	497
Oregon	Ogle	1,600	.00	.8	285
Park Ridge	Cook	1,425	.00	1.0	820
Peru	La Salle	1,500	.00	4.0	1,730
River Forest	Cook	1,000	.08	.1	452
Rochelle	Ogle	1,026	.00	.1	337
Roseville	Warren	1,260	.00	.0	566
				1.4	2,596
Rockdale[a]	Will	657	.00	.4	527
Spring Valley	Bureau	1,400	.00	.1	770
Sycamore	Dekalb	905	.00	2.2	340
Toulon	Stark	1,465	.00	.0	1,147
Warren	Jo Daviess	865	.00	.1	379
Wyoming	Stark	1,557	.00	Trace	1,047

[a]Not city supply.

cased only 100 feet and the pumps were started for the purpose of taking the sample, water from some upper stratum also may have entered the well. The other water, from a 1,000-foot well at River Forest contained very little manganese. The content of iron of these

supplies ranged from 0.0 to 4.0 parts per million, and dissolved solids from 285 to 2,977 parts. Manganese, then, is evidently absent from most waters in St. Peter sandstone in Illinois, and no relation appears to exist between the contents of manganese, iron, and dissolved mineral matter.

WELLS IN LIMESTONE

Tests of samples from 27 wells entering limestone are given in Table 19. Manganese was found in water from wells at Flora, Marion, Matteson, and San Jose, although not more than 0.08 part per million is found in any of the waters examined. Such small amounts are without practical significance. The content of iron ranges from 0.0 to 4.8 parts per million and dissolved solids from 255 to 3,395 parts. Manganese, then, is occasionally found in small amounts in water from wells drawing chiefly from limestone, but it is usually absent.

TABLE 19.—CONTENT OF MANGANESE, IRON, AND DISSOLVED SOLIDS IN WATER FROM WELLS ENTERING LIMESTONE.

[Parts per million.]

Locality.	County.	Depth.	Manganese (Mn).	Iron (Fe).	Dissolved solids.
		Feet.			
Anna	Union	650	0.00	0.0	347
Barrington	Cook	325	.00	.4	397
Carbondale	Jackson	410	.00	.1	2,198
Do	do	610	.00	.4	3,395
Fairfield	Wayne	200	.00	.4	905
Flora	Clay	240	.08	.0	145
Forreston	Ogle	300	.00	.0	610
Highland Park[a]	Lake	395	.00	.0	490
Lake Forest[a]	do	242	.00	.2	255
Leland	La Salle	280	.00	4.8	337
Libertyville	Lake	128	.00	.1	712
Manteno	Kankakee	60	.00	.4	678
Marion	Williamson	700	.04	.6	1,801
Do	do	700	.00	.4	1,110
Do	do	700	.04	.2	1,127
Do	do	800	.05	.2	1,562
Do	do	960	.06	.3	1,535
Matteson	Cook	283	.04	4.0	718
Morris	Grundy	650	.00	.0	434
		800			
Mount Morris	Ogle	500	.00	.1	500
Pecatonica	Winnebago	20	.00	.1	336
San Jose	Mason	105	.08	.0	539
Steger	Will	318	.00	1.0	465
Trenton	Clinton	235	.00	.8	980
Villa Grove	Douglas	629	.00	.0	591
West Chicago	Dupage	322	.00	.8	405
North Crystal Lake	McHenry	285	.00	.3	344

[a]Not city supply.

WELLS IN UNCONSOLIDATED DEPOSITS

Fifty-seven waters from wells in unconsolidated deposits were examined. (See Table 20.) The unconsolidated deposits of Illinois

TABLE 20.—CONTENT OF MANGANESE, IRON, AND DISSOLVED SOLIDS IN WATER FROM WELLS IN UNCONSOLIDATED DEPOSITS.

[Parts per million.]

Locality.	County.	Depth.	Manganese (Mn).	Iron (Fe).	Dissolved solids.
		Feet.			
Arlington Heights	Cook	125	0.00	0.2	751
Arthur	Moultrie	75	.00	2.2	491
Bement	Piatt	141	.04	1.5	547
Bloomington	McLean	100	.00	.1	768
Braidwood	Will	20	.08	.3	492
Camp Point[a]	Adams	40	.12	..	825
Canton[a]	Fulton	10	1.10	.6	194
Carlyle[a]	Clinton	25	2.80	26.0	...
Champaign	Champaign	160	.00	2.0	389
Chillicothe	Peoria	35	.00	.3	504
Crystal Lake	McHenry	32	.00	.06	444
Danville[a]	Vermilion	150	.00	1.5	431
Do [a]	do	150	.00	.4	420
Duquoin	Perry	30	1.50	.2	1,066
Edwardsville[a]	Madison	55—80	.5	1.8	252
Eureka	Woodford	90	.08	3.0	509
			.20		719
Freeport	Stephenson	40	.28	.7	432
Gibson City	Ford	55	.04	.1	320
Grand Ridge	La Salle	196	.12	.8	328
Greenview	Menard	80	.50	1.0	655
Havana	Mason	75	.08	.0	202
Henry	Marshall	40	.00	.0	518
Jacksonville	Morgan	30	.00	1.7	515
Do	do	35	.00	2.0	424
Do	do	35	.00	1.8	372
Keithsburg	Mercer	35	.16	.3	1,262
Lacon	Marshall	50	.00	.0	400
LaHarpe	Hancock	43—63	.12	10.0	515
LaRose[a]	Marshall	28	.12	3.0	500
Lawrenceville[a]	Lawrence	30	.00	.0	424
Do [a]	do	15	.08	.1	309
Do [a]	do	30	.00	.1	273
Do [a]	do	11	.08	.2	340
Do [a]	do	13	.00	.1	279
Do [a]	do	20	.00	.1	377
Lexington	McLean	115	.00	1.0	400
Lovington[a]	Moultrie	147	.08	1.3	548
Mansfield	Piatt	214	.04	2.1	390
Marengo	McHenry	14	.04	.1	392
Mount Sterling[a]	Brown	53	.28	.3	698
Neoga	Cumberland	16	.00	.0	299
Pekin	Tazewell	80—128	.00	.1	465
Peoria	Peoria	60	.16	.0	394
Do	do	60	.44	.0	303
Do	do	60	1.60	.1	302
Do	do	60	.75	.3	270
Do	do	60	.75	.6	289
Do	do	90	.08	.0	413
Roanoke	Woodford	30	.06	.9	900
Rushville	Schuyler	20	.24	.2	362
Sheffield	Bureau	50	.20	.1	505
Springfield	Sangamon	45	.60	2.0	325
Staunton	Macoupin	20	.12	.0	325
Tolono	Champaign	140	.00	1.3	647
Urbana	do	160	.00	2.0	380
Washington	Tazewell	80—90	.00	2.4	367
Woodstock	McHenry	85	.00	2.6	403

[a]Not city supply.

may be divided mainly into two classes; glacial drift is material deposited by glaciers in their movement over the State; alluvium is material deposited by rivers. Carefully recorded records of the strata penetrated by wells are necessary in order to determine whether wells near large rivers are in glacial drift or in alluvium. The mineral mat-

ter in water from wells in alluvium may not represent exclusively mineral matter extracted from alluvium, for part or all of the water that circulates in alluvium may have entered from contiguous beds of glacial material. Few wells from which waters were examined penetrate alluvium only, and available data regarding several wells did not permit precise classification of the materials as glacial drift in distinction from alluvium. All the wells in this group have, therefore, been designated wells in unconsolidated deposits with distinction between alluvium and glacial drift. The content of manganese of these 57 waters ranges from 0.0 to 2.8 parts per million. Twenty-two, or 39 per cent, contain more than 0.10 part per million, and 9, or 16 per cent contain 0.5 part per million or more. The results obtained are plotted in Figure 1. Waters from unconsolidated deposits in the eastern part of the State contain little or no manganese, those containing the large amounts are in the western part. The waters with the greatest content of manganese are near the rivers; 10 of the 13 waters that contain more than 0.2 part per million of manganese are from wells in flood plains or terraces of rivers. The analyses of the 17 waters from wells in flood plains or terraces have been grouped in Table 21. As 12 of the 17 reveal contents of more than 0.2 part per million of manganese it seems that wells in unconsolidated deposits near rivers are more likely to contain manganese than those in unconsolidated deposits elsewhere.

TABLE 21.—CONTENT OF MANGANESE, IRON, AND DISSOLVED SOLIDS IN WATER FROM WELLS IN UNCONSOLIDATED DEPOSITS NEAR RIVERS.

[Parts per million.]

Locality.	County.	Depth.	River.	Manganese (Mn).	Iron (Fe).	Dissolved solids.
		Feet.				
Carlyle	Clinton	25	Kaskaskia	2.8	26.0	...
Chillicothe	Peoria	35	Illinois	.00	.3	504
Edwardsville	Madison	55	Mississippi	.5	1.8	252
		80				
Freeport	Stephenson	40	Pecatonica	.28	.7	432
Havana	Mason	75	Illinois	.08	.0	202
Keithsburg	Mercer	35	Mississippi	.16	.3	1,262
Lacon	Marshall	50	Illinois	.00	.0	400
Peoria	Peoria	60	do	.16	.0	394
Do	do	60	do	.44	.0	303
Do	do	60	do	1.60	.1	302
Do	do	60	do	.75	.8	270
Do	do	60	do	.75	.6	289
Do	do	90	do	.08	.0	413
Canton	Fulton	10	do	1.10	.6	194
Henry	Marshall	40	do	.00	.0	518
Rushville	Schuyler	20	do	.24	.2	362
Springfield	Sangamon	45	Sangamon	.60	2.0	325

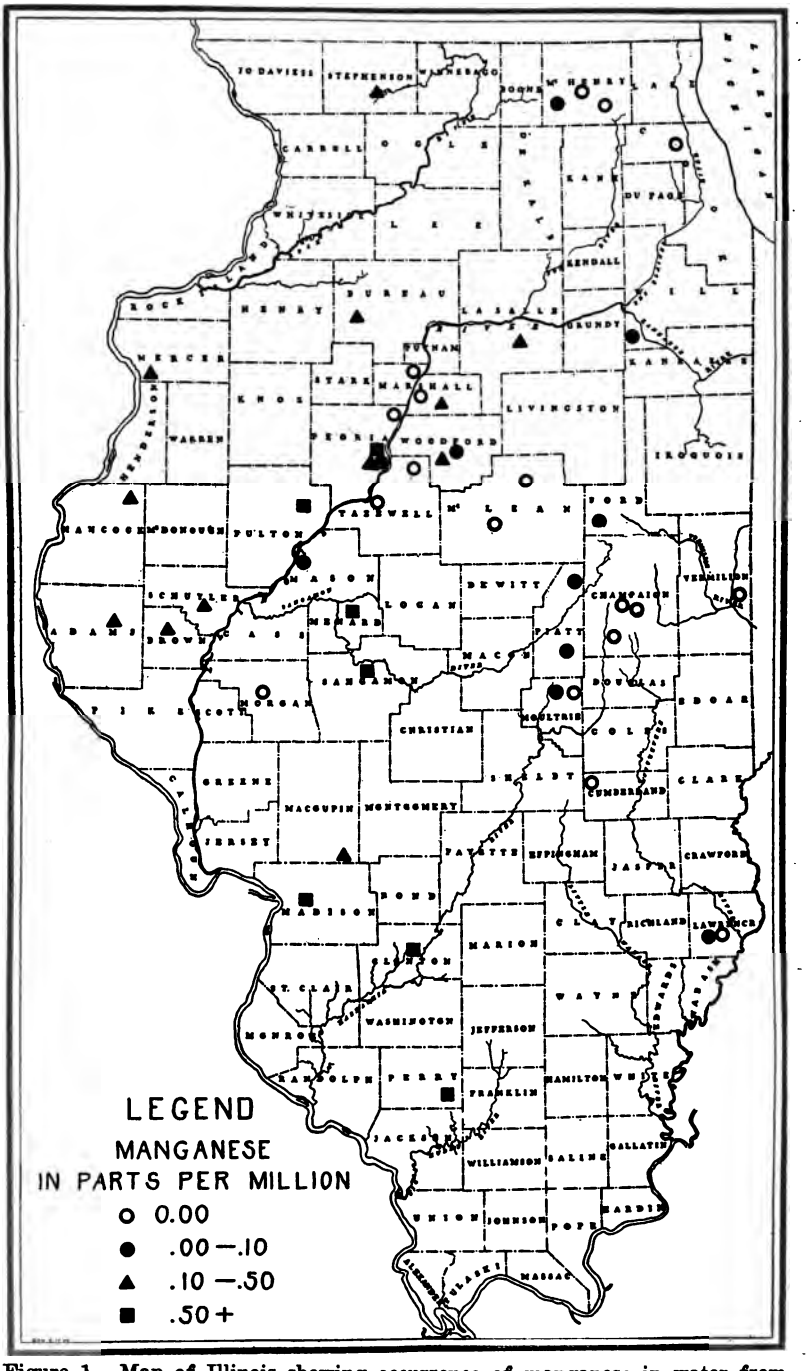


Figure 1.—Map of Illinois showing occurrence of manganese in water from wells in unconsolidated deposits.

The great difference in content of manganese of water from five 60-foot wells within a few hundred feet of one another at Peoria is rather striking. The content of manganese of water from these wells ranges from 0.16 to 1.6 parts per million, and other mineral constituents also present similar differences. The percentages of manganese are shown in Table 22. Though no data concerning the normal content of manganese of unconsolidated material are available the content of these samples does not seem unusual, but it may be sufficiently great to account for the occurrence of manganese in waters circulating in the deposits. No apparent relation exists between the contents of manganese, iron, and total mineral matter of these waters.

TABLE 22.—MANGANESE IN BORINGS FROM TEST WELLS IN UNCONSOLIDATED DEPOSITS AT PEORIA.

Number of well.	Depth of sample.	Content of manganese.
	Feet.	*Per cent.*
2	0— 8.5	0.21
7	3.5—18	.30
78	0— 5	.57
78	5— 8.5	.46
78	8.5—19.5	.56
78	19.4—24.2	.31
119	0— 5.5	.46
119	5.5— 7.5	.22
119	7.5— 9	.23
119	21.6—coal	.23

TABLE 23.—CONTENT OF MANGANESE, IRON, AND DISSOLVED SOLIDS IN WATER FROM SPRINGS.[a]

[Parts per million.]

Locality.	County.	Manganese (Mn).	Iron (Fe).	Dissolved residue.
Ashland	Cass	0.00	1.8	490
Camp Point	Adams	.40	1.2	876
Harrisburg	Saline	.12	2.8	281
Jacksonville	Morgan	.00	.0	378
Kewanee	Henry	.16	2.4	541
Oregon	Ogle	.00	.5	402
Do	do	.00	.2	449
Mount Vernon	Jefferson	7.80	51.2	1,189
Sailor Springs	Clay	.00	8.4	1,272
Taylorville	Morgan	.00	.0	368

[a]None of these springs is used as a public water supply.

SPRINGS

The 10 waters from springs that were examined show wide range in content of manganese. (See Table 23.) Six samples contained none, 3 contained 0.4 part per million or less, and one contained 7.8 parts per million. The water from Green Lawn Spring at Mount Vernon has a greater content of manganese than that from the spring

at Excelsior Springs, Mo., which contains 4.5 parts per million.[1] The water contains no bicarbonates or free sulphuric acid, and the iron and manganese are reported as sulphates.

A surface water at Mount Vernon (see Table 25.) also contains 0.12 to 0.80 part per million of manganese. Water from a well at Camp Point, where the water of next greatest content of manganese is situated, contains 0.12 part per million of manganese. (See Table 20.)

TABLE 24.—CONTENT OF MANGANESE, IRON, AND DISSOLVED SOLIDS IN WATER FROM COAL MINES.

[Parts per million.]

Locality.	County.	Source.	Manganese (Mn).	Iron (Fe).	Dissolved solids.
Duquoin	Perry	Abandoned mine	0.24	0.1	1,160
Danville	Vermilion	Seepage from stripping mine	17.0	5.0	...
Harrisburg	Saline	Mine	56.0	..	7,339
Ladd	Bureau	Abandoned mine	1.3	2.8	3,144
Streator	La Salle	do	1.4	126.5	1,379
Do	do	Stobb's mine	2.0	57.5	2,245

COAL-MINE DRAINAGE

Coal-mine drainage usually contains iron and often large amounts of it, and such drainage is often acid because of hydrolysis of salts of iron and precipitation of iron hydroxide. The iron is derived from pyrite, marcasite, sulphide-bearing shales, and other compounds of sulphur, which are leached by water containing oxygen, and oxidized to ferrous sulphate, a compound soluble in water. Though manganese has not been considered a constituent of mine water examination of 6 samples (See Table 24) of coal-mine drainage shows that all contain manganese and that some contain large amounts. The content of manganese of one sample, which contained free acid when it was analyzed was 56 parts per million. All the samples of mine drainage contained large amounts of dissolved mineral matter, but none except that from Harrisburg contained free acid. No report of such large amounts of manganese in mine water has come to the writer's attention. No trace of manganese could be found even in one-gram samples of pyrite, marcasite, and shale from mines in the Streator district. A sulphide shale, which occurs with the coal in the stripping mine at Danville, where water containing 17 parts per million of manganese was found, contained 1.10 per cent of manganese. Manganese probably is leached from minerals by mine drainage in a manner similar to the removal of iron.

[1] Mason, W. P., The manganese waters of Excelsior Springs: Chem. News, 61, 128 (1890).

TABLE 25.—CONTENT OF MANGANESE, IRON, AND DISSOLVED SOLIDS IN WATER FROM LAKES AND STREAMS.

[Parts per million.]

Locality.	County.	Source.	Manganese (Mn).	Iron (Fe).	Dissolved solids.
Anna	Union	Reservoir on	.0	.6	170
		Kohler Creek	7.5	1.0	214
Belleville	St. Clair	Mississippi River	0.02	0.1	234
Benton	Franklin	Reservoir on creek	.12	3.5	282
Cairo	Alexander	Ohio River	.00	.1	150
					240
Carlinville	Macoupin	Macoupin Creek	.00	.1	317
Centralia	Marion	Crooked Creek	.20	.1	...
Chicago	Cook	Lake Michigan	.00	.0	151
Danville	Vermilion	Vermilion River	.00	.0	309
			.02	.1	454
Decatur	Macon	Sangamon River	.00	.0	305
				.1	375
East St. Louis	St. Clair	Mississippi River	.02	.1	230
Effingham	Effingham	Little Wabash River	.00	.1	235
Evanston	Cook	Lake Michigan	.00	.0	158
Fort Sheridan	do	do	.00	.0	162
Glencoe	do	do	.00	.0	155
Granite City	Madison	Mississippi River	.02	.1	218
Greenup	Cumberland	Embarrass River	.00	.05	681
Hamilton	Hancock	Mississippi River	.00	.0	160
				.1	274
Harrisburg	Saline	Saline River	.32	.8	671
Highland Park	Lake	Lake Michigan	.00	.05	140
Jacksonville[a]	Morgan	Morgan Lake	.00	1.6	1,041
Kankakee	Kankakee	Kankakee River	.04	.1	377
Kangley[a]	La Salle	Vermilion River	4.00	150.0	2,210
Kenilworth	Cook	Lake Michigan	.00	.0	192
Lake Forest	Lake	do	.00	.0	177
Lawrenceville	Lawrence	Embarrass River	.02	.1	575
					1,054
Lowell[a]	La Salle	Vermilion River	7.50	66.0	2,316
Madison	Madison	Mississippi River	.02	.1	224
Moline	Rock Island	do	.00	.1	191
Mount Carmel	Wabash	Wabash River	.00	.1	300
Mount Vernon	Jefferson	Reservoir	.12	.1	215
			.8	.8	402
Do	do	Casey Fork	.00	.1	155
North Chicago	Lake	Lake Michigan	.00	.0	164
Oblong[a]	Crawford	Creek	.36	1.0	1,353
Olney	Richland	Fox River	.04	.7	145
Oglesby[a]	La Salle	Vermilion River	9.00	46.5	2,325
Pontiac	Livingston	do	.00	.05	447
			.08	.2	557
Pullman	Cook	Lake Michigan	.00	.0	151
Quincy	Adams	Mississippi River	.00	.1	222
			.02		250
Rock Island	Rock Island	do	.02	.1	224
Staunton	Macoupin	Cahokia Creek	.16	.1	550
Streator	La Salle	Vermilion River	.00	.0	848
Venice	Madison	Mississippi River	.02	.1	234
Waukegan	Lake	Lake Michigan	.00	.0	184
West Hammond	Cook	do	.00	.0	146

[a]Not city supply.

RIVERS AND LAKES

No manganese was found in any of the waters from Lake Michigan (See Table 25), and not more than 0.02 part was found in any of the samples from Mississippi, Ohio, Wabash, and Sangamon Rivers. Samples from Fox and Embarrass Rivers contained only small amounts. The water of Vermilion River below Streator contains 4 to 9 parts per million of manganese, and much larger amounts of iron,

as shown by analyses of samples collected at Kangley, Lowell, and Oglesby. Samples taken at Streator above the dam at the waterworks contained no manganese or iron. This river below Streator is heavily polluted with mine drainage containing iron and manganese, a condition that explains the high content of manganese and iron. The presence of 0.32 part per million of manganese in the city supply of Harrisburg which is taken from Saline River, is also due to the entrance above the city of coal-mine drainage of high content of manganese.

Many impounding reservoirs on small creeks in southern Illinois like the supplies at Anna, Benton, Centralia, and Mount Vernon, contain manganese. Such reservoirs are fed partly by springs, which may contribute the manganese. Their content of manganese widely varies. At Anna a variation from 0.2 to 7.5 parts per million from July, 1914 to May, 1915, was observed, and at Mount Vernon from 0.1 to 0.8 part per million during the same period. The occurrence of such amounts of manganese in surface waters nearly saturated with dissolved oxygen is contrary to past conceptions of the occurrence of the element. In fact, much experimental work on the removal of manganese has been based on the theory that aeration oxidizes the manganous salt to an insoluble hydrated oxide, which can be removed by filtration.

SUMMARY

Manganese as a constituent of water supplies in the United States has been overlooked and its importance underestimated. It occurs normally in certain classes of water in Illinois, and amounts sufficient seriously to affect the quality have been found in several waters. This may be said of the water supplies at Mount Vernon, Anna, Centralia, Peoria, Springfield, Freeport, and Harrisburg.

Little manganese is present in water from Potsdam sandstone, St. Peter sandstone, the overlying limestones, Lake Michigan, and the large rivers.

Manganese is usually present and often in very large amounts in coal-mine drainage.

Manganese is present in water from some impounding reservoirs on small streams in southern Illinois, and from some wells entering unconsolidated deposits near rivers.

No apparent relation exists between the content of manganese of a water and any of the other mineral constituents.

REMOVAL OF MANGANESE FROM WATER SUPPLIES

Methods

The experimental work which has been done on the removal of manganese from water has led to the development of three practical methods—aeration and filtration through sand, filtration through permutit, and filtration through pyrolusite. The problem of removing manganese has been attacked by most workers in a manner similar to that of removing iron. The usual method for the removal of iron from water is by aeration followed by filtration through sand, and it is generally and successfully used in many plants in the United States and Europe. Iron occurs in most ground waters in the ferrous condition. When the water is aerated the iron is oxidized to the ferric condition and separates as the hydroxide. This combination of oxidation, hydrolysis, and precipitation is the basic principle of the method though the presence of other substances somewhat affects the results. The occurrence of manganese with iron in many waters and its separation as the hydrated dioxide under certain conditions have led to the assumption that the element in water has chemical properties practically similar to those of iron.

Extensive experiments on removal of manganese by this method have been conducted by Thiesing,[1] who worked with a water at Pommerensdorf, Germany. He has concluded that manganese occurring in water as the bicarbonate can be successfully removed by aeration and filtration. Trickling through beds of coke or spraying through nozzles were used as methods of aeration. The removal of carbon dioxide as well as solution of oxygen was found to be important in the process of aeration. Subsequent filtration through sand gave an effluent containing very little manganese, sedimentation effected little removal.

In this country extensive experiments along similar lines have been conducted by R. S. Weston[2] with several waters containing iron and manganese in Massachusetts. Mr. Weston's problems have dealt chiefly with the removal of iron. A well water containing 0.73 part per million of iron and 0.23 part per million of manganese was treated at Cohasset by being sprayed through nozzles followed by passage through a coke trickling filter and mechanical filters. Satisfactory results were obtained in the experiments and arrangements have been made for construction of a large plant. In experiments at Brookline

[1]Thiesing, [Experiments on the removal of manganese from ground water]: Mitt. kgl. Prüfungsans. Wasserversorgung, 16, 210-96 (1912).

[2]Weston, R. S., The purification of ground waters containing iron and manganese: Trans. Am. Soc. C. E., 64, 112-81 (1909); Some recent experiences in the deferrization and demanganization of water: J. N. E. Water Works Assoc., 28, 27-59 (1914).

sprinkling through nozzles followed by passage through a coke trickling filter and slow sand filters decreased the content of iron from 0.6 to 0.2 part per million. The content of manganese of the untreated water was 0.26 part per million, though Weston published no figures concerning the efficiency of the removal of manganese he stated that he found it roughly proportional to that of the removal of iron. A plant for removal of iron and manganese, which has been installed at Middleboro, treats 335,000 gallons a day of water. The water, after it has been sprayed over a coke trickling filter 10 feet deep, flows into a settling basin and through slow sand filters operating at a rate of 10,000,000 gallons per acre per day. The content of iron was decreased from 1.5 to 0.2 part per million and the content of manganese from 0.67 to 0.27 part per million during the first run from September 26, 1913, to January 12, 1914. The efficiency of the removal of manganese increased as the plant was operated longer, and the effluent on January 22 contained 0.10 part per million of manganese.

Barbour[1] performed a similar series of experiments on the well-water supply of Lowell, Mass. The waters of the wells differ in content of manganese, the strongest containing 2.0 parts per million. Aeration, sedimentation, and sand filtration were tried on an experimental scale. The efficiency of the plant was at first rather erratic, but it finally became possible to reduce the content of manganese to 0.01 part per million. A dark coloration due to precipitated oxides of manganese was observed in the sand bed, and this extended in diminishing amounts to the bottom of the bed. On the basis of this study a plant was erected at a cost of $180,000 for the removal of manganese and iron.

Practically all students of removal of manganese by aeration and filtration have concluded that manganese is much more difficult to remove than iron. The details of the process, such as the amount of aeration and the rate of filtration, differ with the character of the water.

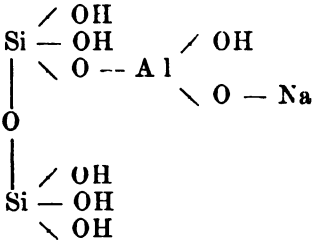
The permutit process for removal of manganese has come recently into the field. Permutit, the artificial zeolite[2] first produced and patented by Gans of the Prussian Geological Institute of Berlin, has come into somewhat common use in softening water. Its use for removing calcium and magnesium from water has been studied by

[1]Barbour, F. A., Removal of carbonic acid, iron, and manganese from the Lowell (Mass.) well-water supply: Eng. Record, 70, 78-9 (1914).

[2]Gans, Robert, [Manufacture of artificial zeolite in crystalline form]: U. S. pat. 914, 405, March 9, 1909, Chem. Rev. Fett-Harz-Ind., 16, 302-3 (1909).
Duggan, T. R., Zeolites, natural and artificial (Abstract): Orig. Com. 8th Intern. Congr. Appl. Chem. (Appendix), 25, 125-9 (1912).
Gans, Robert. Ueber die technische Bedeutung der Permutite (der künstlichen zeolithartigen Verbindungen): Chem. Ind., 32, 197-200 (1909).

numerous investigators. Gans, however, has adapted it to the removal of manganese from water. The principles involved in this latter process are decidedly different from those involved in ordinary processes of softening water.

Sodium permutit is made by fusing together 3 parts of kaolin, 6 parts of sand, and 12 parts of soda. The melt, after cooling, is leached with water. Gans[1] proposes the following to represent sodium permutit.



The sodium in this compound is replaceable by other metals. For example, when a solution of a compound of calcium percolates through the crushed material, the calcium replaces the sodium in the silicate, is removed from the solution, and is in turn replaced in the water by an equivalent of sodium. On the other hand, when a solution of a a compound of sodium is filtered through the calcium permutit the calcium is forced out by the sodium. The process may be simply represented by the equilibria:

$$\overset{++}{Ca} + 2Na\text{-permutit} = 2\overset{+}{Na} + Ca\text{-permutit.}$$

$$\overset{++}{Mg} + 2Na\text{-permutit} = 2\overset{+}{Na} + Mg\text{-permutit.}$$

Thus, if a hard water percolates through sodium permutit, the calcium and magnesium in the water are replaced by sodium. If, after this change is complete, a solution of sodium chloride percolates through the used permutit the calcium and magnesium therein are replaced and removed by sodium. The permutit is thus regenerated, or restored, to its original condition without loss. The series of reactions constitutes an apt application of the law of mass action. Permutit is not lost unless the water contains free carbon dioxide, which has on the permutit a solvent action that results in the formation of bicarbonate.

Gans[2] noted that manganese can be removed with compounds of

[1]Gans, Robert. Ueber die technische Bedeutung (der Permutite der künstlichen zeolithartigen Verbindugen): Chem. Ind., 32, 197-200 (1909).

[2]Gans, Robert, Reinigung des Trinkwassers von Mangan durch Aluminatsilicate: Chem. Ztg., 31, 855-6 (1907).

calcium and magnesium when a manganese-bearing water is filtered through the zeolite. Usually, however, it is desired to remove only the manganese without the extra expense of softening the water. To accomplish this, Gans[1] treated permutit with a strong solution of manganous chloride or sulphate, and then with a strong solution of a permanganate. He found that if a water containing manganese or iron is filtered through this medium, the manganese and iron could be removed without the accompanying softening action. After a time the filter medium no longer effected removal, but its efficiency was restored by regenerating it with permanganate. The chemistry of this process is explained by Gans.[1] Treatment with manganous chloride gives a manganese zeolite.

$$2SiO_2 \cdot Al_2O_3 \cdot CaO + MnCl_2 = 2SiO_2 \cdot Al_2O_3 \cdot MnO + CaCl_2$$

When this zeolite is treated with permanganate, the following reactions may take place:

(a) $2SiO_2 \cdot Al_2O_3 \cdot MnO_2 + CaMn_2O_8 \; 2SiO_2 \cdot Al_2O_3 \cdot CaO + MnO \cdot Mn_2O_7.$

(b) $2(SiO_2 \cdot Al_2O_3 \cdot MnO) + H_2O + CaMn_2O_8 = \left\{ \begin{matrix} 2SiO_2 \cdot Al_2O_3 \cdot CaO \\ 2SiO_2 \cdot Al_2O_3 \cdot H_2O \end{matrix} \right\} + 2MnO \cdot Mn_2O_7.$

(c) $3(SiO_2 \cdot Al_2O_3 \cdot MnO) + 2H_2O + CaMn_2O_8 = \left\{ \begin{matrix} 2SiO_2 \cdot Al_2O_3 \cdot CaO \\ 2SiO_2 \cdot Al_2O_3 \cdot H_2O \\ 2SiO_2 \cdot Al_2O_3 \cdot H_2O \end{matrix} \right\} + 3MnO \cdot Mn_2O_7.$

The precipitation of manganese by these zeolites, which depends on the action of the oxides of manganese, is represented by the following reactions:

(a) $2(MnO \cdot Mn_2O_7) + 3Mn(HCO_3)_2 = 5MnO \cdot 2Mn_2O_7 + 6CO_2 + 3H_2O$

(b) $2MnO \cdot Mn_2O_7 + 3Mn(HCO_3)_2 = 5MnO \cdot Mn_2O_7 + 6CO_2 + 3H_2O$

(c) $2(3MnO \cdot Mn_2O_7) + 9Mn(HCO_3)_2 = 15MnO \cdot 2Mn_2O_7 + 18CO_2 + 9H_2O$

Gans[2] successfully applied the process at Glogau to a water that contained 1.5 to 2.0 parts per million of manganese. The free carbon dioxide was first removed by passing the water through crushed marble. The treated water was free from manganese and neutral. The hardness was slightly increased by solution of calcium in the neutralization of free carbon dioxide. Iron is removed with the manganese in the process. As the cost of installation of a permutit plant is high it has been introduced in only a few places for large-scale operations.

[1] Gans, Robert, Die Mangangefahr bei der Benutzung von Grundwasser zur Trinkwasserversorgung und deren Beseitigung: Chem. Ind., 33, 48-51, 66-9 (1910).

[2] Oesterr. Chem. Tech. Ztg. 26, Bohrtechnicker section 15, 178.

The oxide, Mn_2O_7, is considered the basis of the removal process in a pamphlet distributed by The Permutit Co. entitled "The chemistry of permutit." The reactions presented are as follows, the letter p representing permutit:

$$p\text{-}Na_2 + MnCl_2 = p\text{-}Mn + 2NaCl$$
$$p\text{-}Mn + 2KMnO_4 = p\text{-}K_2MnO : Mn_2O_7$$
$$p\text{-}K_2MnO.Mn_2O_7 = p\text{-}K_23MnO + 5O$$

The question of whether the reduction is to MnO, MnO_2, or Mn_2O_3 is considered in this discussion to be undecided.

Another method of removing manganese was patented by Pappel[1] who filtered the manganese-bearing water through granular pyrolusite. The material finally may lose its power of removal, but the power is restored by washing it with ordinary tap water. Though this process was investigated experimentally at Dresden by Schmeitzner[2] it was not adopted there for use on a large scale. Manganese is removed from the city supply of Breslau by this method. A natural sand containing pyrolusite is used as the medium.

Tillmans and Heublein,[3] who studied the theory of removal of manganese by this method, found that when pieces of pyrolusite were allowed to stand suspended in tubes containing a solution of manganous sulphate solidified with gelatin, after which ammonia was poured on the surface, the Liesegang rings in the vicinity of the pieces of pyrolusite were absent. The power of this substance to absorb and remove manganous salts from solutions was thus shown. When pure manganese dioxide was allowed to react with a dilute solution of manganous sulphate the free acid formed was equivalent to the manganese removed. They consider the reaction to be:

$$MnO_2 + MnSO_4 = Mn_2O_3 + SO_3$$

Tillmans,[4] reviewing his former work in a later article states that manganese dioxide is the essential medium which removes manganese in the permutit process.

Other methods for the removal of manganese have been proposed, in which chemicals to precipitate the element are added to the water. Lührig and Blasky,[5] who were among the first to experiment on this

[1]Pappel, Alfred, Entmanganen von Wasser, German pat. 241, 571: Chem. Ztg. Rep., 36, 7 (1912).

[2]Schmeitzner, R., [The removal of manganese from ground water]: Techn. Gem. bl., 15, 343; Wasser u. Abwasser, 7, 376-7 (1914); through C. A. 8, 974 (1914).

[3]Tillmans, J., and Heublein, O., Versuche zur Theorie der Entmanganung von Grundwasser: Z. Nahr. Genussm., 27, 253-64 (1914).

[4]Tillmans, J., Über die Entmanganung von Trinkwasser: J. Gasbel., 57, 713-24 (1914).

[5]Lührig, H., and Blasky, A., Mangan im Grundwasser der Breslauer Wasserleitungen und die Frage der Abscheidung des Mangansulfates aus demselben: Chem. Ztg., 31, 255-7 (1907).

problem, suggested the addition of potassium permanganate or lime to precipitate the manganese. These chemical methods have not come into practical use. A study of them was undertaken by the writer to determine the chemistry of the processes and especially that in which the water is treated by aeration.

Manganese Permutit

Specimens of manganese permutit, kindly furnished by The Permutit Co. for the study, consist of irregular black grains 2 or 3 millimeters in diameter. When these are crushed, a white core is noted in the center of each. A specimen of the permutit was ground, dried at 105°C., and analyzed. Manganese was determined as the pyrophosphate. Available oxygen was determined by distilling the chlorine evolved on treatment with hydrochloric acid into potassium iodide and titrating the liberated iodine. The analysis is as follows:

TABLE 26.—ANALYSIS OF MANGANESE PERMUTIT.

Potassium oxide (K_2O)	4.00
Sodium oxide (Na_2O)	4.37
Calcium oxide (CaO)	1.87
Magnesium oxide (MgO)	.17
Ferric oxide (Fe_2O_3)	.42
Alumina (Al_2O_3)	22.72
Silica (SiO_2)	38.28
Manganous oxide (MnO)	10.37
Available oxygen (O)	1.94
Water	15.34
	99.48

This specimen of permutit had been prepared by treating sodium permutit with manganous salt and afterward with potassium permanganate. The determined content of manganese, calculated as MnO, is 10.37 per cent; the amount of available oxygen, which should determine the degree of oxidation of the manganese, was found to be 1.94 per cent. The theoretical percentage of available oxygen which should have been obtained if the manganese had been present in each form is as follows:

	Available Oxygen (O).
MnO_2 for 10.37 per cent of MnO as—	2.37
Mn_2O_3	1.17
Mn_3O_4	.78
MnO	none.

As 1.94 per cent of available oxygen was found, the oxide is higher than MnO, Mn_3O_4, and Mn_2O_3, but not so high as MnO_2.

In order to determine what compounds of manganese effected the removal specimens of ground manganese permutit were regenerated to the greatest possible degree, and exhausted to the least possible degree. One portion was treated with a saturated solution of potassium permanganate and agitated in a shaking machine, for several days. It was then allowed to stand for two weeks, at the end of which time the solid material was removed by filtration, washed free from permanganate, dried, and analyzed. The composition was as follows:

TABLE 27.—ANALYSIS OF SPECIALLY TREATED MANGANESE PERMUTIT.

Potassium oxide (K_2O)	10.26
Sodium oxide (Na_2O)	1.00
Calcium oxide (CaO)	1.28
Magnesium oxide (MgO)	trace
Ferric oxide (Fe_2O_3)	.66
Alumina (Al_2O_3)	22.62
Silica (SiO_2)	39.09
Manganous oxide (MnO)	12.30
Available oxygen (O)	2.49
Water	10.83
	100.53

The empirical formula calculated from the above analysis is $3R_2O \cdot 3MnO_x \cdot 4Al_2O_3 \cdot 12SiO_2 \cdot 11H_2O$, in which R_2O represents the oxides of the alkalies and alkaline earths. After regeneration the amount of manganese calculated as MnO was found to be 12.30 per cent, and the available oxygen, 2.49 per cent. The theoretical quantity of available oxygen, if all the manganese had been in the form of MnO_2, would have been 2.77 per cent. This shows that regeneration has increased the available-oxygen ratio, or the degree of oxidation of the manganese, but that it is still somewhat lower than the theoretical for manganese dioxide.

There are several reasons why a quantity of available oxygen smaller than the theoretical might be obtained. The treatment may not have been continued sufficiently long to complete the reaction. All the manganese which is present in an insoluble silicate of this character probably can not be reached and attacked by the permanganate because of the physical structure of the material. Moreover, Morse, Hopkins, and Walker[1] have shown that manganese dioxide loses a

[1]Morse, H. N., Hopkins, A. J., and Walker, M. S., The reduction of permanganic acid by manganese superoxide: Am. Chem. J., 18, 401-19 (1896).

small quantity of its oxygen on drying in the air and that compounds like $MnO:5OMnO_2$ are obtained. For this reason a content of available oxygen slightly lower than actually present would be found by analysis.

The large percentage of potassium and the small percentages of sodium, calcium, and magnesium compared with the smaller percentage of potassium and the larger percentages of sodium, calcium, and magnesium found before regeneration in this specimen are particularly interesting. This is explained by the fact that these metals are replaceable, and that treatment with potassium permanganate has not only brought about oxidation of the manganese, but has at the same time effected replacement of the other metals with potassium. The effect of replacement can be represented graphically by the reaction:

$$(K, Na, Ca)\ Permutit + 3K^{+}MnO_4^{-} = K_x\ Permutit + Ca^{++}(MnO_4^{-})_2 + Na^{+}MnO_4^{-}$$

Oxidation of the manganese in the zeolite takes place with the replacement, giving manganese dioxide as the limit of oxidation and not such higher oxides as $MnO \cdot Mn_2O_7$ and $2MnO \cdot Mn_2O_7$, as suggested by Gans.[1]

A portion of this regenerated sample was then shaken with a strong solution of manganous sulphate in the same manner. After washing and drying it was found to have the composition shown in Table 28.

TABLE 28.—ANALYSIS OF SPECIALLY TREATED REGENERATED MANGANESE PERMUTIT.

Potassium oxide (K_2O)	3.15
Sodium oxide (Na_2O)	2.20
Calcium oxide (CaO)	.54
Magnesium oxide (MgO)	Trace
Ferric oxide (Fe_2O_3)	.50
Alumina (Al_2O_3)	23.05
Silica (SiO_2)	37.37
Manganous oxide (MnO)	15.05
Available oxygen (O)	2.00
Water	14.76
	99.62

The empirical formula calculated from this analysis is, $3/2\ R_2O \cdot 4MnO_x : 4Al_2O_3 \cdot 12SiO_2 \cdot 16H_2O$.

[1] Gans, Robert, Die Mangangefahr bei der Benutzung von Grundwasser zur Trinkwasserversorgung und deren Beseitigung: Chem. Ind., 33, 48-51, 66-9 (1910).

The determined content of available oxygen was 2.00 per cent. The theoretical content of available oxygen for Mn_2O_3, the oxide next lower than MnO_2, is 1.70 per cent. It was subsequently found, however, that in the analysis of the reduced material, oxygen was taken up while the substance was being dried in the air. The content of 2.00 per cent, therefore, is probably too great, and little significance should be attached to it.

The low percentages of sodium and potassium, and the high percentage of manganese are interesting, especially when they are compared with corresponding figures for the regenerated specimen. A replacement as well as a reduction again has taken place. The replacement is the substitution of manganese for the sodium and potassium of the permutit, which can be represented by the reaction:

$$K_2 \text{ Permutit} + \overset{++}{Mn}\overset{--}{SO_4} = Mn \text{ Permutit} + \overset{+}{K_2}\overset{--}{SO_4}$$

The extent to which this reaction takes place is governed by the concentration of manganese in the solution. As the concentration is usually very low this reaction is relatively unimportant and it must take place to only very slight extent. Coincident with this reaction the manganese dioxide is reduced to a lower oxide by the manganous salt thus: $MnO_2 + MnSO_4 => Mn_2O_x + SO_3$. This is the basic reaction involved in the permutit process.

The acid which is formed when the manganese is removed is undoubtedly neutralized by the alkaline silicate, for Gans[1] has shown that free acid, even carbonic acid, has a solvent action on permutit.

Manganese permutit consists of a zeolite with which a layer of manganese dioxide is incorporated. When a manganese-bearing water is filtered through this medium the manganese is removed from the water by the formation of a lower oxide of manganese by reaction between the manganese in the water and the manganese dioxide in the permutit. At the same time the alkali or alkaline-earth of the silicate is replaced by the manganous compound of the water. The replacement is of minor importance, and the slight extent to which it takes place is dependent on the concentration of manganese in the water. Manganese is added to the permutit not only when manganese permutit is regenerated by potassium permanganate but also when manganese is removed from water by the regenerated permutit; therefore, the content of manganese dioxide increases and the filter medium approaches in composition pure manganese dioxide with each successive regeneration and reduction. As the zeolite can not increase in amount

[1] Idem.

with successive reductions and regenerations the replacement effect must become less and less as the substance is used. These conclusions are in entire accord with that reached independently by Tillmans[1]—that the action of manganese permutit is really the action of manganese dioxide.

Sand Filtration

Some preliminary experiments made by filtering an aerated artificially prepared manganese-bearing water through a small sand filter showed that no removal of manganese was effected. A mechanical filtration plant has been installed at Mount Vernon, Ill., however, for the

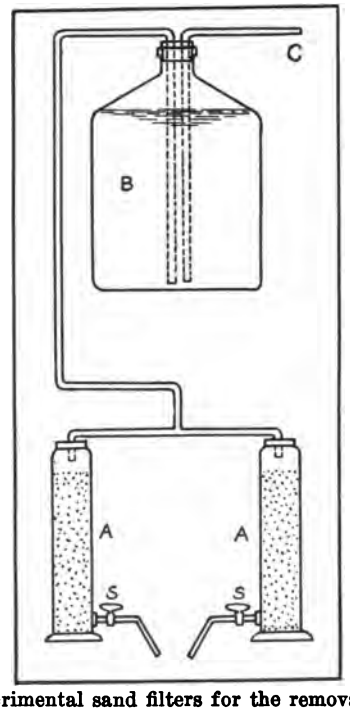


Figure 2.—Experimental sand filters for the removal of manganese.

purpose of removing manganese as well as effecting hygienic purification of a surface water, and analyses of the water some months after installation of the mechanical filters showed that manganese was being removed by this plant. Manganese is also removed in a filter plant at Anna, Ill., designed for hygienic purification of a surface-water supply. These results seemed contradictory to the negative results obtained on a small scale. Yet, as manganese dioxide had been used

[1]Tillmans, J., Über die Entmanganung von Trinkwasser: J. Gasbel., 57, 713-24 (1914).

successfully for removal of manganese and as this compound is the basic part of manganese permutit it was concluded that manganese dioxide was the principal factor in the removal of manganese in successful sand filtration.

Two filters were, therefore, prepared for experimental use. The apparatus (See Figure 2) consisted of two gas-washing cylinders (A, A) connected at their tops by a siphon to a large carboy (B) holding the water to be treated. The rate of filtration could be so adjusted by two stopcocks (S, S) that both filters would deliver their effluents at the same rate. A glass tube (C) extending to the bottom of the carboy provided means for admitting compressed air for aeration.

Each filter was filled with one liter of clean high-grade filter sand, having an effective size of 0.50 millimeter and a uniformity coefficient of 1.32. One filter was treated successively with solutions of manganous sulphate, sodium hydroxide, and potassium permanganate. After two or three treatments a thin film of black oxide of manganese had formed on the grains of sand. The filter was then washed with water until an effluent free from manganese was obtained. The other filter was used without such treatment. The apparatus consisted, therefore, of two filters working in parallel, one containing sand only, and the other containing sand which had been slightly coated with manganese dioxide. As the depth of sand in each was 35 centimeters the filtering area of each was 28 square centimeters.

The removal of manganese in a manganese-removal filter, depends on the contact of the manganous compound with manganese dioxide; consequently, the rate of filtration should be expressed in terms of volume of water filtered per volume of filter medium and not per area of filter surface. The rate varied slightly in these experiments, but it was so adjusted that a volume of water equal to the volume of the filter medium was filtered in twenty minutes. The waters used were prepared by dissolving compounds of iron and manganese in tap water, distilled water, and a mixture of the two. The tap water is a bicarbonate, iron-bearing water from drift wells. The determinations in Table 29 represent the character of the tap water used in reference to a discussion of removal of manganese.

TABLE 29.—CHARACTER OF TAP WATER USED IN EXPERIMENTATION ON REMOVAL OF MANGANESE.

	Parts per million.
Turbidity	5
Color	15

Residue on evaporation	370
Chloride	.3
Alkalinity as $CaCO_3$ in presence of methyl orange	355
Free carbon dioxide	40
Iron	2.0
Manganese	none
Total hardness	300
Dissolved oxygen	none
Oxygen consumed	4.8

The first artificial water was prepared by adding 5 parts per million of manganese as $MnSO_4 \cdot 4H_2O$ to a mixture of about equal parts of tap water and distilled water. The water was aerated by blowing air through it for one hour and allowing to stand for two hours. It was then filtered through the apparatus, and manganese, iron, carbon dioxide, dissolved oxygen, and alkalinity, were determined in samples taken at two-hour intervals. The results are shown in Table 30.

TABLE 30.—REMOVAL OF MANGANESE BY AERATION AND FILTRATION OF A MIXTURE OF TAP WATER AND DISTILLED WATER CONTAINING 5 PARTS PER MILLION OF MANGANESE.

[Parts per million.]

Determinations.	Unfiltered water.	Water filtered through—	
		Sand.	Sand coated with manganese dioxide.
AT START			
Manganese	4.8	4.4	.0
Iron	.4	.05	.0
Alkalinity	200	200	196
Dissolved oxygen	7.4	7.2	6.2
Carbon dioxide	4.0	2.0	2.0
AFTER 2 HOURS' OPERATION			
Manganese	4.8	4.8	.0
Iron	.4	.05	.0
Alkalinity	200	200	194
Dissolved oxygen	7.2	7.4	6.6
AFTER 4 HOURS' OPERATION			
Manganese	4.8	4.4	.0
Iron	.4	.05	.0
Alkalinity	200	200	194
Dissolved oxygen	7.4	7.4	6.6
Carbon dioxide	2.0	4.0	6.0
AFTER 6 HOURS' OPERATION			
Manganese	4.8	4.0	.05
Iron	.4	.05	.0
Alkalinity	200	200	192
Dissolved oxygen	7.5	7.5	6.8

Aeration decreased the content of free carbon dioxide to 2 to 4 parts per million, and increased the content of dissolved oxygen to 7.4 parts per million. Filtration through sand removed practically all the iron, but caused practically no change in the content of manganese, dissolved oxygen, and alkalinity. Filtration through sand coated with manganese dioxide, on the other hand, removed all manganese and iron, has decreased the content of dissolved oxygen an average of .8 part per million and the alkalinity an average of .4 part per million. These results indicate that aeration and sand filtration do not remove appreciable amounts of manganese. In the manganese-dioxide filter the manganous compound evidently combines with the manganese dioxide to form a lower oxide exactly as in the pyrolusite and the permutit processes. When manganese is removed the equivalent of free acid that is formed causes a corresponding decrease in the alkalinity. This decrease should theoretically be 10 parts per million when 5 parts per million of manganese is removed, whereas the actual decrease was only 4 parts per million. The disappearance of 0.8 part per million of dissolved oxygen in the manganese-dioxide filter is undoubtedly due to oxidation of the lower oxide of manganese to manganese di-

TABLE 31.—REMOVAL OF MANGANESE BY AERATION AND FILTRATION, OF TAP WATER CONTAINING 10 PARTS PER MILLION OF MANGANESE.

[Parts per million.]

Determinations.	Unfiltered water.	Water filtered through—	
		Sand.	Sand coated with manganese dioxide.
AT START			
Manganese	10.5	9.0	0.1
Iron	.8	.0	.0
Alkalinity	356	354	342
Dissolved oxygen	5.3	3.4	5.0
Carbon dioxide	4	6	8
AFTER 2 HOURS' OPERATION			
Manganese	10	10.5	.1
Iron	.8	.0	.0
Alkalinity	358	356	344
Dissolved oxygen	5.6	4.2	4.1
Carbon dioxide	6	8	12
AFTER 4 HOURS' OPERATION			
Manganese	9.5	10.0	.0
Iron	.8	.1	.0
Alkalinity	358	358	342
Dissolved oxygen	5.6	4.0	4.0
AFTER 6 HOURS' OPERATION			
Manganese	10.0	10.0	.0
Iron	.8	.0	.0
Alkalinity	356	354	340
Dissolved oxygen	5.7	4.5	3.5

oxide. If this were quantitative the removal of 5 parts of manganese should reduce the content of dissolved oxygen 1.6 parts; the actual reduction was, however, only 0·8 part.

In another series of experiments (See Table 31) tap water in which 10 parts per million of manganese as $MnSO_4 \cdot 4H_2O$ had been dissolved was used.

These results are generally similar to those in Table 30. Filtration through sand removed iron, but did not detectibly decrease manganese. The content of dissolved oxygen was decreased throughout more than one part per million by passage through the filters, even in the experiment in which no removal of manganese apparently took place. Filtration through sand coated with manganese dioxide removed all manganese and iron, decreased alkalinity 14 parts per million, and decreased dissolved oxygen about the same extent to which it was decreased in the sand filter.

In order to determine the effect of adding a coagulant, 2 grains per gallon of alum was added to the artificial water, the water was then aerated, and allowed to settle one hour as in the other series. The results obtained (See Table 32) indicate that little change is caused

TABLE 32.—REMOVAL OF MANGANESE BY AERATION AND FILTRATION, OF ARTIFICIAL WATER CONTAINING 5 PARTS PER MILLION OF MANGANESE AND 2 GRAINS PER GALLON OF ALUM. ALKALINITY BEFORE TREATMENT 356 PARTS.

[Parts per million.]

Determinations.	Unfiltered water.	Water filtered through—	
		Sand.	Sand coated with manganese dioxide.
AT START			
Manganese	5.0	4.8	0.0
Iron	.2	.0	.0
Alkalinity	340	340	328
Dissolved oxygen	8.0	6.5	6.5
AFTER 2 HOURS' OPERATION			
Manganese	5.0	4.7	.0
Iron	.2	.0	.0
Alkalinity	338	338	330
Dissolved oxygen	8.0	7.2	6.0
AFTER 4 HOURS' OPERATION			
Manganese	5.0	4.8	.0
Iron	.2	.05	.0
Alkalinity	340	338	328
Dissolved oxygen	8.0	7.0	6.2
AFTER 6 HOURS' OPERATION			
Manganese	4.8	5.0	.0
Iron	.2	.2	.0
Alkalinity	336	334	330
Dissolved oxygen	7.5	7.0	6.0

by addition of the coagulant. Complete removal of manganese was obtained by filtration through sand coated with manganese dioxide but practically no removal by filtration through sand alone.

The action in presence of both iron and manganese was studied by treating a mixture of distilled water and tap water in which 10 parts per million of manganese as $MnSO_4 \cdot 4H_2O$ and 10 parts per million of iron as $FeSO_4 \cdot (NH_4)_2SO_4 6H_2O$ had been dissolved (See Table 33). After this water had been aerated it had a high reddish-brown turbidity caused by precipitated ferric hydroxide. Treatment of this solution by filtration through sand alone resulted in complete removal of iron but no removal of manganese. Treatment of it by filtration through sand coated with manganese dioxide, however, completely removed manganese and iron. The alkalinity was not decreased by passage through either filter; this is not in accordance with the theory as the removal should have decreased the alkalinity by an amount equivalent to the manganese removed. This apparent discrepancy might be accounted for either by the presence of small amounts of substances capable of neutralizing free acid in the sand, or by oxidation of the manganous compound to a marked degree in the aeration and yet to a degree insufficient to form an insoluble compound.

TABLE 33.—REMOVAL OF MANGANESE BY AERATION AND FILTRATION OF A MIXTURE OF TAP WATER AND DISTILLED WATER CONTAINING 10 PARTS PER MILLION OF MANGANESE AND 10 PARTS PER MILLION OF IRON.

[Parts per million.]

Determinations.	Unfiltered water.	Water filtered through—	
		Sand.	Sand coated with manganese dioxide.
AT START			
Manganese	10.0	10.0	0.0
Iron	5.0	.1	.0
Alkalinity	24	26	30
Dissolved oxygen	7.8	7.4	2.9
AFTER 2 HOURS' OPERATION			
Manganese	9.5	10.0	.0
Iron	4.8	.0	.0
Alkalinity	24	24	30
Dissolved oxygen	7.6	7.5	2.8
AFTER 4 HOURS' OPERATION			
Manganese	9.0	10.0	.0
Iron	5.0	.0	.0
Alkalinity	22	24	30
Dissolved oxygen	7.6	7.8	6.0
AFTER 6 HOURS' OPERATION			
Manganese	10.0	9.0	.0
Iron	4.8	.0	.0
Alkalinity	24	24	28
Dissolved oxygen	7.6	7.8	7.0

Though no removal of manganese by filtration through sand could be detected by analysis the upper part of the sand became discolored by a slight deposit of manganese dioxide after the filter had been used for some time. This shows that there must have been some slight but continual removal of manganese by aeration and filtration. This slight deposit would rapidly aid in removal of more and more manganese until sufficient manganese dioxide would have been deposited to remove completely the manganese from water filtered through it; the process might be erroneously considered to be simply one of aeration and filtration through sand when in reality it is a catalysis by manganese dioxide.

Manganese-Removal Plants in Illinois

Manganese is efficiently removed from surface-water supplies by filtration through sand coated with manganese dioxide at two plants in Illinois. One of these filter plants was installed for removal of manganese as well as for hygienic purification of the water, and the other was installed for hygienic purification only, the presence of manganese in the water not being suspected. There was evidence of unsatisfactory removal of manganese for some time after the installation of these plants, but efficient removal resulted after a period had elapsed for the deposition of sufficient manganese dioxide in the filters. As no similar observations have been reported a description of these two plants with some of the operating results are presented.

REMOVAL OF MANGANESE AT ANNA.

The waterworks of Anna State Hospital, in southern Illinois, are located about 2 miles from Anna and about 3½ miles from the hospital buildings. The plant was put in operation in January, 1914.

About half the supply is derived from a 2,000,000-gallon impounding reservoir, on Kohler Creek, which is fed by springs which bubble up over the bottom of the reservoir as well as by rainfall on the watershed. The other half of the supply used is taken from Wilson Creek, a near-by stream.

Mineral analyses of these two sources of supply are given in Table 34.

The supply from Wilson Creek contains practically no manganese, but that from the reservoir contains a large amount.

The content of manganese of water from the reservoir varies widely. Turbidity, color, and bacterial content are low compared with those of other surface waters of Illinois. The water contains much

TABLE 34.—MINERAL ANALYSES OF THE WATER SUPPLY OF ANNA STATE HOSPITAL, OCTOBER, 1914.

[Parts per million.]

	Wilson Creek.	Reservoir.
IONS		
Potassium (K)	5.6	4.7
Sodium (Na)	17.8	11.8
Magnesium (Mg)	12.6	7.5
Calcium (Ca)	78.6	43.9
Iron (Fe)	1.0	0.6
Manganese (Mn)	Trace	1.4
Alumina (Al_2O_3)	1.2	3.0
Silica (SiO_2)	18.2	6.3
Nitrate (NO_3)	5.3	4.0
Chloride (Cl)	3.0	1.0
Sulfate (SO_4)	5.2	11.1
HYPOTHETICAL COMBINATIONS		
Potassium nitrate (KNO_3)	8.6	6.5
Potassium chloride (KCl)	6.3	2.1
Potassium sulfate (K_2SO_4)	....	2.4
Sodium sulfate (Na_2SO_4)	7.7	14.5
Sodium carbonate (Na_2CO_3)	35.2	10.8
Magnesium carbonate ($MgCO_3$)	43.6	26.0
Calcium carbonate ($CaCO_3$)	196.2	109.8
Iron carbonate ($FeCO_3$)	2.0	1.2
Manganese carbonate ($MnCO_3$)	Trace	2.9
Alumnia (Al_2O_3)	1.2	3.0
Silica (SiO_2)	18.2	6.3
Bases	2.0	0.0
Total	321.0	185.5

dissolved oxygen and very little carbon dioxide. Determinations showed 9.8 parts per million of dissolved oxygen, which is high, but only 3 parts per million of carbon dioxide when the temperature of the water was 20°C. The water is treated by ordinary mechanical filtration. About one grain per gallon of alum is added, after which the water passes through a sedimentation basin affording retention for 4 hours. Calcium hypochlorite is added at the outlet of the sedimentation basin at the rate of 0.2 part per million of available chlorine, after which the water passes to the filters. There are 3 concrete filter units, each having a capacity of 300,000 gallons per 24 hours. The nominal rate of filtration is 125,000,000 gallons per acre per day. The filters contain 9 inches of gravel and 30 inches of sand, which had, when it was put in place, an effective size of 0.55 millimeter and a uniformity coefficient of 1.43.

The presence of manganese in a surface water containing so much dissolved oxygen was not suspected until complaint was received that the filtered water was causing unsightly stains on white plumbing fixtures and was staining fabrics in the laundry a pale yellow. A content of 12 parts per million of manganese was found in the raw water July 22, 1914. Subsequent tests showed that the untreated water from the impounding reservoir contained 7.5 parts, July 30, and only

1.4 parts, October 5. The water of Wilson Creek contained 0.05 part July 30 and a trace October 5. The effluent from the filters contained 0.05 part July 30 and 0.0 part October 5. The analyses of raw and filtered water indicate an efficient removal of manganese by the treatment which the water received. In order to determine the cause of this removal the plant was visited in December, 1914, and it was arranged to have determinations of manganese made regularly in the laboratory of the waterworks.

It was impossible to obtain representative samples of the raw water, as the supplies from both reservoir and Wilson Creek enter the settling basin through separate inlets in such manner that thoroughly mixed samples can not be obtained until they emerge from the basin. Determinations of manganese in the water from the reservoir were made from December 1 to February 11, and one-half of this value was taken as the true content of manganese of the raw water used. Determinations were made, however, from February 11 to May 4 on the water at the outlet of the settling basin. It was found that the content of manganese of water at this point was about half that of water from the reservoir. As the determinations were made by the persulphate method on 50-cubic centimeter samples only figures in the first decimal place are significant. The results obtained on samples from December 1 to May 4 are shown in Table 35.

Manganese could be detected in the filtered water in only 7 of the 100 tests. The water applied to the filters during this period had a content of manganese of 0.0 to 1.0 part per million; the removal is, therefore, very efficient. The content of manganese of the reservoir supply has been slowly decreasing since the summer of 1914. In March and April, 1915, the content was 0.2 to 0.6 part per million, whereas in December, 1914, it was 1.0 to 2.0 parts per million. In order to determine the effect, if any, of treatment with hypochlorite on the removal of manganese the application of that chemical was omitted from May 1 to 4, 1915. As an effluent free from manganese was obtained during this period as before it seems apparent that as good results were obtained without as with bleach.

The walls of the concrete filter units were covered with a layer of manganese dioxide, which in appearance resembled asphaltum paint.

Samples of the filter sand were collected for examination. The sand was black although the incrustation was not sufficient greatly to increase the size of the grains. The incrustation was somewhat tenacious, but some of it became detached when the sand was stirred with

TABLE 35.—CONTENT OF MANGANESE OF RESERVOIR, RAW, AND FILTERED WATER AT ANNA STATE HOSPITAL.

[Parts per million.]

Date.	Reservoir water.	Raw water.	Filtered water.	Date.	Reservoir water.	Raw water.	Filtered water.
1914				1915			
Dec. 1	1.5	0.7	0.2	Mar. 1	.4	.2	.0
2	2.0	1.0	.2	2	.4	.1	.0
3	1.0	.5	.0	3	.5	.2	.2
5	1.2	.6	.1	4	.6	.4	.0
7	1.4	.7	.0	5	.4	.2	.0
9	.8	.4	.0	6	.4	.2	.1
11	1.2	.6	.0	8	.6	.4	.1
13	1.4	.7	.0	9	.4	.2	.0
15	1.2	.6	.0	10	.2	.0	.0
17	1.8	.9	.0	11	.2	.0	.0
19	1.9	1.0	0	12	.2	.0	.0
21	1.7	.8	.0	15	.4	.2	.1
23	1.1	.6	.0	16	.4	.1	.0
29	2.0	1.0	.0	17	.6	.2	.0
31	1.7	.9	.0	18	.4	.2	.0
				19	.4	.1	.0
				20	.5	.3	.0
				22	.4	.2	.0
1915				23	.2	.1	.0
Jan. 1	1.6	.8	.0	24	.2	.1	.0
3	1.8	.9	.0	25	.2	.0	.0
5	2.1	1.0	.0	26	.4	.2	0
7	2.2	1.1	.0	27	.2	.0	.0
9	2.1	1.1	.0	29	.2	.1	.0
11	2.1	1.1	.0	30	.3	.2	.0
13	1.9	.9	.0	31	.3	.0	.0
15	1.8	.9	.0				
17	1.7	.9	.0	1915			
19	1.6	.8	.0	Apr. 1	0.2	0.1	0.0
21	1.6	.8	.0	2	.2	.0	.0
23	1.4	.7	.0	3	.1	.0	.0
25	1.4	.7	.0	5	.2	.2	.0
27	1.6	.8	.0	6	.3	.1	.0
29	1.8	.9	.0	7	.3	.0	.0
31	1.9	1.0	.0	8	.3	.1	.0
				9	.4	.2	.0
				10	.4	.2	.0
				12	.4	.1	.0
				13	.3	.1	.0
1915				14	.3	.1	.0
Feb. 1	1.6	0.8	0.0	15	.4	.2	.0
3	1.4	.7	.0	16	.3	.0	.0
5	1.2	.6	.0	17	.5	.3	.0
7	1.6	.8	.0	19	.4	.0	.0
9	.8	.4	.0	20	.5	.3	.0
11	.5	.3	.0	21	.4	.2	.0
13	.4	.2	.0	22	.3	.1	.0
15	.2	.1	.0	23	.4	.2	.0
[a]17	.0	0	.0	24	.5	.3	.0
[a]19	.0	.0	.0	26	.3	.2	.0
21	.2	1	.0	27	.4	.3	.0
23	.2	.0	.0	28	.4	.2	.0
25	.2	1	.0	29	.5	.3	.0
27	.3	.1	.0	30	.3	.1	.0
				1915			
				May 1	.3	.1	.0
				3	.6	.4	.0
				4	1.0	.5	.0

[a]Heavy rains.

water. The results of a soil analysis of the sand are given in Table 36. Microscopic examination of the sediment washed from the sand grains as well as of the sediment from the water used in washing the filters showed the presence of diatoms and algae, but no organisms

resembling *Crenothrix* were found. The material consisted chiefly of debris, such as sand, clay, and precipitated hydroxides of manganese, iron, and aluminium.

TABLE 36.—ANALYSIS OF FILTER SAND, ANNA STATE HOSPITAL.

Insoluble in hydrochloric acid	98.25
Soluble in hydrochloric acid	1.75
Loss on ignition	.91
The soluble portion consists of:	
Ferric oxide (Fe_2O_3)	16.8
Alumina (Al_2O_3)	26.5
Manganese dioxide (MnO_2)	12.0
Loss on ignition	54

The presence of manganese dioxide in the incrustation on the filter sand is sufficient to account for the removal of the manganese from the water. Some experiments were undertaken, however, to determine whether manganese dioxide was the only factor in the process. The two experimental filters, one containing sand and the other sand impregnated with manganese dioxide, which had been used in the former experimental work with artificially prepared waters, were used at Anna for filtering the raw water. The raw water contained 9.6 parts per million of dissolved oxygen and 3 parts per million of free carbon dioxide. Its temperature was 20°C. The results obtained are shown in Table 37. Complete removal of manganese was obtained when the filter containing manganese dioxide was used, but only slight removal of manganese was obtained when the filter containing sand alone was used. This filter, however, had been used for similar work previously, and a small amount of manganese dioxide that may have been present on the sand grains doubtless aided the removal.

TABLE 37.—REMOVAL OF MANGANESE BY FILTRATION OF RAW WATER AT ANNA STATE HOSPITAL THROUGH EXPERIMENTAL FILTERS OF SAND AND OF SAND ARTIFICIALLY COATED WITH MANGANESE DIOXIDE.

[Parts per million of manganese.]

Raw water.	Water filtered through—	
	Sand.	Sand coated with manganese dioxide.
1.0	0.8	0.0
1.0	1.0	.1
1.0	.9	.0
1.0	.9	.0

In order to test the theory more completely the raw water was filtered through another pair of filters, one containing some unused sand like that with which the large filters at Anna are filled and the other containing sand from the filters which had been used nearly a year. The latter sand was coal black due to the coating of manganese dioxide which had formed on the grains. The results of these experiments are shown in Table 38. Complete removal of manganese was obtained with the used sand, and practically no removal was obtained with the unused sand.

TABLE 38.—REMOVAL OF MANGANESE BY FILTRATION OF RAW WATER AT ANNA STATE HOSPITAL THROUGH EXPERIMENTAL FILTERS OF UNUSED SAND AND OF SAND AFTER USE NATURALLY COATED WITH MANGANESE DIOXIDE.

[Parts per million of manganese.]

Raw water.	Water filtered through—	
	Unused sand.	Used sand.
1.0	1.0	0.0
1.0	1.2	.0
1.0	1.0	.0
1.0	1.0	.0

The city of Dresden, Germany, has installed[1] a manganese-removal plant, in which the water is filtered through a growth of manganese-depositing microorganisms that remove the manganese from the water. No microorganisms of this character could be detected by microscopic examination of the filter sand and the sediment in the wash water from the plant at Anna. In order to test the possibility of their significance in the removal, however, some of the black sand which had been in use for several months and was removing the manganese was sterilized in the autoclave. A filter was prepared from

TABLE 39.—REMOVAL OF MANGANESE BY FILTRATION OF A SOLUTION OF 5 PARTS PER MILLION OF MANGANESE IN DISTILLED WATER THROUGH AN EXPERIMENTAL FILTER OF STERILIZED USED SAND.

[Parts per million of manganese.]

Raw water.	Water filtered through—	
	Unused sand.	Used sand sterilized.
5.0	4.8	0.0
5.0	5.0	.0
5.0	5.0	.0
5.0	5.0	.0

[1] Vollmar, D., Die Entmanganung des Grundwassers im Elbtale und die für Dresden ausgeführten Anlagen: J. Gasbel., 57, 944-8, 956-9 (1914).

this sterilized sand, and after it had been washed until it was free from manganese it was used to filter a solution of 5 parts per million of manganese as $MnSO_4 \cdot 4H_2O$ in distilled water. The results, in Table 39, show that complete removal of manganese was obtained by filtration through the sterilized sand.

The results of these experiments prove conclusively that the deposit of manganese dioxide on the grains of sand effects the removal of manganese. The deposit, however, has been formed gradually by the slow deposition of manganese from the manganese-bearing water assisted by direct oxidation by the dissolved oxygen. The large amount of dissolved oxygen always present in the raw water evidently oxidizes the lower oxide of manganese to the dioxide at the time the manganese is removed. The process is, therefore, catalytic and no regeneration is necessary. When the filter is washed the grains of sand are stirred up, and the friction probably is sufficient to scour off the coating of manganese dioxide sufficiently to prevent difficulty in operation of the plant.

REMOVAL OF MANGANESE AT MOUNT VERNON

Mount Vernon, a city of approximately 8,000 population, is in the central part of Jefferson County, Illinois. The water supply is

TABLE 40.—MINERAL ANALYSES OF THE WATER SUPPLY OF MOUNT VERNON.

[Parts per million.]

	Casey Fork.	Reservoir.
IONS		
Potassium (K)	7.6	8.3
Sodium (Na)	9.3	13.1
Magnesium (Mg)	10.0	17.6
Calcium (Ca)	13.2	23.3
Iron (Fe)	.1	1.6
Manganese (Mn)	Trace	1.15
Alumina (Al_2O_3)	2.0	1.0
Silica (SiO_2)	17.4	7.0
Nitrate (NO_3)	6.0	2.7
Chlorine (Cl)	3.0	5.0
Sulphate (SO_4)	62.1	130.8
Bases	5.4	3.8
HYPOTHETICAL COMBINATIONS		
Potassium nitrate (KNO_3)	9.8	4.4
Potassium chloride (KCl)	6.3	10.5
Potassium sulphate (K_2SO_4)	.9	2.2
Sodium sulphate (Na_2SO_4)	28.7	40.0
Magnesium sulphate ($MgSO_4$)	49.4	87.0
Calcium sulphate ($CaSO_4$)	3.5	45.8
Calcium carbonate ($CaCO_3$)	30.5	24.5
Iron carbonate ($FeCO_3$)	.2	3.3
Manganese carbonate ($MnCO_3$)	Trace	2.3
Alumina (Al_2O_3)	2.0	1.0
Silica (SiO_2)	17.4	7.0
Bases	5.4	3.8
Total	154.1	231.8

TABLE 41.—CONTENT OF MANGANESE OF RAW AND FILTERED WATER AT MOUNT VERNON.

[Parts per million.]

Date.	Raw water.	Filtered water.	Date.	Raw water.	Filtered water.
1914			1915		
Jan. 9	0.4	0.2	Feb. 16	0.4	0.0
Feb. 16	.4	.25	18	.5	.1
Mar. 24	.5	.1	20	.4	.0
July 23	.05	.05	23	.5	.0
Aug. 18	.12	.12	25	.5	.0
Oct. 14	.4	.0	28	.4	.0
Dec. 2	.4	.0	Mar. 2	.4	.1
5	.4	.0	4	.4	.1
7	.4	.0	6	.4	.1
9	.4	.0	15	.4	.0
11	.4	.0	18	.4	.1
14	.6	.2	20	.3	.0
16	.6	.2	23	.3	.0
19	.7	.1	25	.3	.0
21	.7	.2	27	.3	.0
23	.8	.1	29	.3	.0
26	.6	.0	31	.2	.0
28	.6	.1			
31	.6	.1			
1915					
Jan. 4	.6	.1	Apr. 2	.3	.1
6	.6	.1	5	.2	.0
9	.6	.0	6	.2	.0
12	.7	.1	8	.2	.0
13	.7	.2	10	.2	.0
15	.8	.2	12	.2	.0
18	.8	.3	13	.2	.0
22	.8	.3	16	.2	.0
23	.8	.2	17	.2	.0
25	.7	.1	22	.3	.0
27	.7	.0	24	.3	.0
29	.6	.0			
Feb. 1	.6	.1			
3	.6	.2			
6	.6	.1			
9	.4	.0			
12	.4	.0			
15	.4	.0			

obtained chiefly from an impounding reservoir fed by springs in the bottom, but Casey Fork, a branch of Big Muddy River, furnishes an auxiliary supply. Water from an impounding reservoir on Casey Fork is pumped into the reservoir which is fed by springs. The mineral character of these two supplies is shown by the analyses in Table 40. Both supplies have a high percentage of saturation with dissolved oxygen. The water is treated with about one-half grain per gallon of alum. After sedimentation it is treated with calcium hypochlorite at the rate of 0.2 to 0.3 part per million of available chlorine. Three concrete filters, each having a capacity of 500,000 gallons a day, operate at a rate of 125,000,000 gallons per acre per day.

The results of determinations of manganese made in the raw and in the filtered water from January, 1914, to April, 1915, are shown in Table 41. The determinations after December 1, 1914, were made in the laboratory of the waterworks at Mount Vernon. The content

of manganese of the untreated water varied rather widely, the range having been from 0.05 to 0.8 part per million during one year. The efficiency of removal of manganese is well shown by comparison of the contents of the raw and filtered waters. The content of manganese of the filtered water has ranged from 0.0 to 0.3 part per million. No manganese was found in the filtered water on 35 of the 65 days on which tests were made.

The filter sand was coated with a dark colored substance, which contained a large amount of manganese. The results of the analysis of the sand are shown in Table 42. When the sand was examined microscopically before being washed no Crenothrix or similar organisms were found. The wash water contained clay, dirt, inert matter, diatoms, chlorophyl-bearing algae, debris, and similar material.

TABLE 42.—ANALYSIS OF FILTER SAND, MOUNT VERNON.

Insoluble in hydrochloric acid	99.01
Soluble in hydrochloric acid	.99
Loss on ignition	.43
The soluble portion consists of:	
Ferric oxide (Fe_2O_3)	4.8
Alumina (Al_2O_3)	27.7
Manganese dioxide (MnO_2)	35.0
Loss on ignition	43

The filter medium used at this plant is, therefore, similar to that used at Anna State Hospital. As the incrustation of the sand is not so great its content of manganese dioxide is somewhat smaller. This fact probably explains the somewhat lower efficiency of removal at Mount Vernon compared with that obtained at Anna State Hospital. The removal is effected, however, in exactly the same process as at the hospital, namely, by filtration through sand coated with a layer of manganese dioxide, which effects the removal.

INCRUSTATION OF WATER PIPES BY MANGANESE-BEARING WATERS

The fact that water which carries only a small amount of manganese will cause serious incrustation of water pipes has been noted by many investigators. The incrustations consist chiefly of oxides of manganese and iron. Weston[1] gives analyses of three such incrustations, collected from the water mains at Hanover, Germany and analyzed by him. The largest amount of manganese present was 7.15

[1]Weston, R. S., The purification of ground waters containing iron and manganese: Trans. Am. Soc. C. E., 64, 112-81 (1909).

per cent. Raumer[1] found an incrustation in the water supply of Fürth which contained 43.85 per cent of Mn_3O_4, equivalent to 10.52 per cent of manganese. The raw water contained 2 parts per million of manganese. Threadlike organisms resembling Crenothrix were found. Other examples of the clogging of pipes by manganese waters are noted by Bailey,[2] Jackson,[3] Beythien, Hempel, and Kraft,[4] Volmar,[5] and others. Most of these investigators attribute the deposition to the growth of iron- and manganese-secreting bacteria which deposit the oxides of these metals in their sheaths.

Similar incrustations, whose composition is reported by Bartow and Corson,[6] have caused serious difficulty in the water supplies of Mount Vernon and Peoria, Illinois. In a microscopic examination of these deposits no organisms resembling Crenothrix could be found. Specimens from the water mains of Mount Vernon, Peoria, Anna, and Springfield contained large amounts of iron and manganese, but none of the oxide-depositing bacteria. These incrustations, moreover, did not present the thread-like, filamentous appearance which is usually characteristic of growths of Crenothrix.

In view of the important catalytic effect of manganese dioxide in processes of removal it seems probable that this substance is responsible for the formation of the incrustations where organisms do not play a part. If a manganese-bearing water containing dissolved oxygen is pumped into the distribution system there is undoubtedly a very slight precipitation of manganese as the hydrated dioxide. This dioxide then reacts with the manganous compound in the water and removes it as a lower oxide. The dissolved oxygen present, however, simultaneously oxidizes this lower oxide to manganese dioxide. The process is, therefore, catalytic, and is exactly the same as that occurring in the removal of manganese in a manganese-dioxide filter. As acid is formed as one of the products of reaction when manganese is removed the hydrogen-ion concentration of the water determines the point at which equilibrium is reached. Free carbon dioxide in solution renders water acid. So-

[1]Raumer, E. von, Ueber das Auftreten von Eisen und Mangan in Wasserleitungswasser: Z. anal. Chem., 42, 590-602 (1903).

[2]Bailey, E. H. S., Occurrence of manganese in a deposit found in city water pipes: J. Am. Chem. Soc., 26, 714-5 (1904).

[3]Jackson, D. D., The precipitation of iron, manganese, and aluminum by bacterial action: J. Soc. Chem. Ind., 21, 681-4 (1902).

[4]Beythien, A., Hempel, H., and Kraft, L., Beiträge zur Kenntnis des Vorkommens von Crenothrix Polyspora in Brunnenwassern: Z. Nahr. Genussm., 7, 215-21 (1904).

[5]Vollmar, D., Die Entmanganung des Grundwassers im Elbtale und die für Dresden ausgeführten Anlagen: J. Gasbel., 57, 944-8, 956-9 (1914).

[6]Corson, H. P., Occurrence of manganese in the water supply and in an incrustation in the water mains at Mount Vernon, Illinois: Illinois Univ. Bull., Water-Survey Series 10, 57-65 (1913).

dium, calcium, and magnesium bicarbonates, on the other hand, render water alkaline because they are hydrolyzed. Both carbon dioxide and bicarbonate are usually present, and whether a water is acid or alkaline depends on the relative amounts of each in the solution. It is clear that the lower the content of free carbon dioxide and the higher the content of bicarbonate, the lower will be the hydrogen-ion concentration, and, therefore, the greater the tendency toward precipitation of manganese.

CONCLUSION

The results of the researches and experimental investigations conducted by the writer on manganese in water and described herein are summarized in the following paragraphs.

The persulphate method is the most convenient and accurate method for the colorimetric determination of manganese in water. Chloride does not interfere. Five-thousandths of a milligram of manganese in a volume of 50 cubic centimeters, equivalent to 0.1 part per million, can be detected.

The standardized bismuthate method is accurate and reliable. The presence of chloride in amounts less than 5 milligrams does not interfere with this determination. By this method 0.01 milligram of manganese in a volume of 50 cubic centimeters, equivalent to 0.2 part per million, can be detected.

The lead-peroxide method gives too low results because of reduction of permanganate in using the Gooch crucible. The presence of chloride interferes in this method more seriously than in either of the others, and if more than 5 milligrams of chloride are present no manganese may be found even if a comparatively large amount is present. This method is at best the least sensitive of the three, and it should be rejected as a standard method.

Manganese occurs normally in certain classes of water in Illinois, and amounts sufficient to affect the quality have been found in several waters.

Little manganese is present in water from "Potsdam" sandstone, St. Peter sandstone, the overlying limestones, Lake Michigan, and the large rivers.

Manganese is usually present in large amounts in coal-mine drainage, in water from some impounding reservoirs on small streams in southern Illinois, and in water from some wells entering unconsolidated deposits near rivers. No apparent relation exists between the content of manganese of a water and any of the other mineral constituents.

The principle underlying all processes for the removal of manganese from water supplies, except those of direct chemical precipitation, is the reaction between manganous compounds and manganese dioxide to form a lower oxide.

The removal of manganese by the permutit process takes place according to this reaction, as the state of oxidation of manganese in the substance is not greater than that in manganese dioxide. This is in agreement with the view of Tillmans. No evidence of the existence of oxides higher than MnO_2 in this substance was found by the writer, contrary to the suggestion of Gans and the Permutit Co.

No appreciable removal of manganese was obtained on an experimental scale by aeration and sand filtration, as reported by Thiesing, Weston, and Barbour. When an artificial coating of manganese dioxide was prepared on the grains of sand, however, complete removal of manganese was obtained. Manganese is efficiently removed from water supplies at Anna and Mount Vernon, Illinois, by this process, a coating of manganese dioxide having formed on the sand. If the water contains dissolved oxygen regeneration of the filter is unnecessary, and the process may be considered catalytic.

The success of the aeration and sand-filtration process used by Thiesing, Weston, and Barbour is in reality due to the action of manganese dioxide and not to aeration and sand filtration alone. The assumption that manganese may be removed by the same process which removes iron is incorrect.

The formation of incrustations of manganese in water pipes, where manganese-secreting bacteria are not present, is explainable by the catalytic action of manganese dioxide.